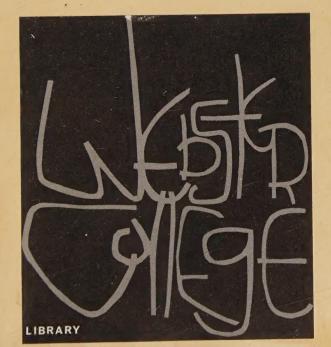
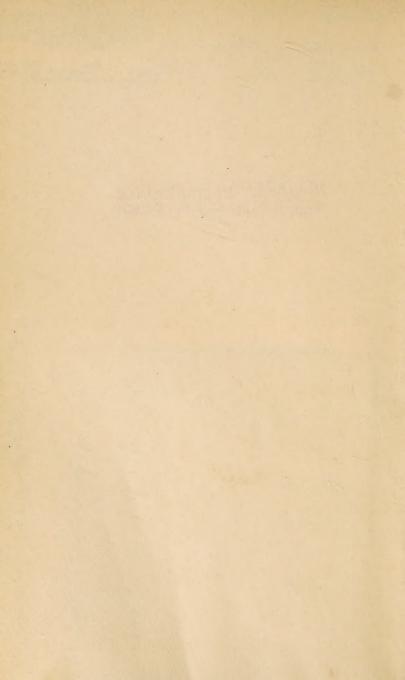




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THE FUNDAMENTALS OF CHEMICAL THERMODYNAMICS



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THE FUNDAMENTALS OF CHEMICAL THERMODYNAMICS

PART II

THERMODYNAMICAL FUNCTIONS
AND THEIR APPLICATIONS

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PREFACE

This volume is concerned with the thermodynamical functions, energy, free energy and entropy, and their partial derivatives. In my experience it is desirable that the student should have some familiarity with the calculation of maximum work and the simpler applications of the first and second laws of thermodynamics before he embarks on the study of these quantities. This I endeavoured to provide in Part I, and my readers will find that they have already met some of these quantities, and in these circumstances the transition to the new

methods will present no great difficulty.

It has been inevitable on this plan that I should cover again, in greater detail and from a more advanced point of view, some of the ground traversed in Part I, but I do not think this will be found to be a disadvantage. The exact distribution of material between the two parts is a matter of expedience, and I can only claim that the arrangement I have adopted has worked well in practice, the material of Part I forming a first course, and that of Part II a second course, which are studied in consecutive years. But this could easily be modified to suit other circumstances. The present volume, however, is tolerably complete in itself and could be read by anyone who has an elementary knowledge of the laws of thermodynamics.

While the method employed is essentially that of Gibbs, I have made extensive use of the partial derivatives introduced by G. N. Lewis, which are essential to the discussion of modern thermodynamics. With certain exceptions, the discussions are brought to the point

of current progress, and I hope that, apart from the primary purpose as a text-book, they will be useful as a reasoned review of progress during the last decade.

The writer on Thermodynamics is bound to encounter the difficulty that while statistical relations are being widely used for the interpretation of thermodynamical data, he is unable to provide a proper basis for their understanding. While I realise that ultimately the study of chemical equilibrium will be based on the twin supports of Thermodynamics and Statistical Mechanics, I have been content for the present to adopt a conservative attitude in this respect, and I have only used a few statistical relations which could not be avoided.

I have again marked with an asterisk certain sections

which may be omitted without loss of continuity.

I am indebted to The Royal Society, The Chemical Society, Sir Harold Hartley, Dr. C. W. Davies, and Prof. H. S. Harned for permission to reproduce diagrams.

King's Buildings, Edinburgh. March, 1934.

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Go, little booke; God send thee good passage, And specially let this be thy prayere Unto them all that will thee read or hear, Where thou art wrong after their help to call, Thee to correct in any part or all.

Geoffrey Chaucer.

CHAPTER I

THERMODYNAMICAL FUNCTIONS

In the elementary theory we were mainly concerned with the energy changes and the maximum work obtained in typical chemical changes. We considered each change by itself, determined by a suitable method the maximum work of which it was capable under any given conditions, and by the use of the laws of thermodynamics were then able to determine the characteristics of the state of equilibrium and to calculate the effect thereon of changes of temperature and pressure. We shall now seek to relate the energy and work changes in physicochemical processes to quantities which have definite values for any given state of a system. Such quantities, some of which have already been introduced, are known as thermodynamical functions. Their use enables many problems to be solved with ease, which would require the consideration of complicated and often clumsy cyclic processes by the methods we have hitherto used.

Energy and Heat Content. The first thermodynamical function of the state of a system is its energy. We have seen that the energy change of a system when it is changed from one state to another is a definite quantity, depending only on the initial state and the final state. We may therefore regard a system as having in any given

в.с.т. п.

or

state a definite quantity of energy E. When the system passes from a state in which its energy is E_1 to a state in which its energy is E_2 , the energy which must come from outside sources is

$$\Delta E = E_2 - E_1$$
.(1)

In general the energy of a system may change by giving heat to or taking heat from other bodies, or by the performance of work against or by the forces acting on it. We may thus write

$$\Delta E = q - w, \dots (2)$$

where q is the heat absorbed by the system, and w the work done by it against the forces acting on it, in any given change. When no work is performed by the system, as in an absorption of heat at constant volume,

$$\Delta E = (q)_v$$
;(3)

i.e. the increase of energy is equal to the heat absorbed.

In dealing with changes at constant pressure, we found it convenient to make use of another quantity H, the heat content. If the system has a uniform pressure p throughout, and a volume v, we may write

$$H = E + pv.$$
(4)

Since p and v, like E, have definite values for any given state, H is also a thermodynamical function of the state of the system. The difference between the values of H in two states of a system, both at the same pressure p, is given, by (4), by

$$H_2 - H_1 = E_2 - E_1 + p(v_2 - v_1),$$

 $\Delta H = \Delta E + p\Delta v.$ (5)

Since $p\Delta v$ is the work done in the increase of volume Δv , against the constant pressure p, it is evident from (2) that the heat absorbed in a reaction at constant pressure is equal to ΔH , *i.e.* we may write

$$\Delta H = (q)_p$$
.(6)

Although the energy of a system in any given state is quite definite, it is impossible to assign to it an absolute value. We can only measure the increase or decrease of energy of the system when it passes from one state to another, and we shall suffer no inconvenience if we arbitrarily define the energy as zero in one particular state. Then the value of the energy in any other state is determined by the amount of energy expended in bringing the system from the state of zero energy into the state in question. The same applies, of course, to the heat content, which is a function of the energy, the pressure and the volume. For some purposes it is convenient to take the heat contents of the chemical elements, each in some particular state of aggregation which has been chosen as the standard state, as zero at a specified temperature. Then the heat content of a given quantity of any compound at the same temperature is determined by the heat absorbed in the formation, at constant pressure, of this amount of the compound from its elements, the latter being initially in the chosen standard state.

The variation of the energy and heat content of a system with temperature are given by the equations:

$$\frac{dE}{dT} = C_v, \quad \frac{dH}{dT} = C_{\mathcal{D}}, \quad \dots (7)$$

where C_v and C_p are the heat capacities of the system at constant volume and constant pressure respectively.

For any change of state, we may therefore write, using the nomenclature of (1),

$$\frac{d(\Delta E)}{dT} = \frac{dE_2}{dT} - \frac{dE_1}{dT} = (C_v)_2 - (C_v)_1 = \Delta C_v; \dots (8)$$

and

$$\frac{d(\Delta H)}{dT} = \frac{dH_2}{dT} - \frac{dH_1}{dT} = (C_p)_2 - (C_p)_1 = \Delta C_p, \dots (9)$$

where $(C_v)_1$, $(C_p)_1$ are the two heat capacities of the system in its initial state and $(C_v)_2$, $(C_p)_2$ its heat capacities in the final state. ΔC_v and ΔC_p are the corresponding differences of heat capacity between the final and the initial states of the system.

The heat capacity of most substances can only be regarded as constant over a limited range of temperature. If, however, the dependence on the temperature of the heat capacities of the substances taking part in the reaction is known, the equations (8) and (9) can be integrated when the proper values of C_p or C_v have been substituted. The relations between heat capacity and temperature are simpler for gases than for solids or liquids, and can in most cases be represented empirically over a considerable range of temperature by equations of the form

$$C_p = a + bT + cT^2 + dT^3...$$
 (10)

Table I. gives equations which represent the molar heat capacities of a number of gases over a very wide range of temperature from 0° C. to from 1000 to 2000° C., according to G. N. Lewis and M. Randall. (These equations are quite empirical; almost any function which varies to a first approximation linearly with T could be represented by a sufficient number of terms of this kind.)

We can obtain ΔC_p for a reaction by subtracting the equations for the reacting gases from those of the products of the reaction, taking note of the amount of each gas which enters into the reaction. Thus we obtain in general an equation of the form

$$\Delta C_p = \alpha + \beta T + \gamma T^2 + \delta T^3 \dots (11)$$

Substituting this value in (9), we have

$$\frac{d(\Delta H)}{dT} = \alpha + \beta T + \gamma T^2 + \delta T^3 \dots,$$

and integrating, we find

$$\Delta H = \alpha T + \frac{\beta}{2} T^2 + \frac{\gamma}{3} T^3 + \frac{\delta}{4} T^4 \dots + \Delta H_0, \dots (12)$$

where ΔH_0 is the integration constant. ΔH_0 is evidently the value of ΔH when T=0, but it cannot be identified with the value of the heat content change at absolute zero, for the heat capacity equations on which (12) is based are never valid at low temperatures in the region of absolute zero. The values of ΔH_0 for some common reactions for use with the data in Table I are given in Table II.

TABLE I.

EMPIRICAL EQUATIONS OF LEWIS AND RANDALL FOR THE HEAT CAPACITY OF GASES.

Monotomic gases; $C_p = 5.0$.

 H_2 ; $C_n = 6.50 + 0.0009T$.

 O_2 , N_2 , NO, CO, HCl, HBr, HI; $C_p = 6.50 + 0.0010T$.

 Cl_2 , Br_2 , I_2 ; $C_p = 7.4 + 0.001T$.

 H_2O , H_2S ; $C_p = 8.81 - 0.0019T + 0.00000222T^2$.

 CO_2 , SO_2 ; $C_p = 7.0 + 0.0071T - 0.00000186T^2$.

 NH_3 ; $C_p = 8.04 + 0.0007T + 0.0000051T^2$.

 CH_4 ; $C_n = 7.8 + 0.005T$.

TABLE II.

Values of ΔH_0 for use with Table I.

			$\Delta \mathbf{H}_0$
$\mathbf{H}_2(g)$	$+1/2\mathrm{O}_2(g)$	$= \mathbf{H}_2 \mathbf{O}(g)$	-57410 calories.
$1/2\mathrm{H}_2(g)$	$+1/2\mathrm{Cl}_2(g)$	=HCl (g)	-21870
$1/2H_{2}(g)$	$+1/2\mathrm{Br_2}(g)$	=HBr (g)	-11970
$1/2\mathrm{H}_2(g)$	$+1/2I_2(g)$	=HI (g)	- 1270
$\mathbf{H}_{2}(g)$	$+1/2S_{2}(g)$	$=\mathrm{H}_{2}\mathrm{S}\left(g\right)$	-19200
$SO_2(g)$	$+1/2O_{2}(g)$	$=SO_3(g)$	-22600
$1/2N_2(g)$	$+1/2O_{2}(g)$	=NO (g)	+21600
NO(g)	$+1/2O_{2}(g)$	$=NO_2(g)$	-14170
$1/2N_2(g)$	$+3/2H_{2}(g)$	$=NH_3(g)$	- 9500
C(graphite)	$+1/2O_{2}(g)$	= CO(g)	-26600
C(graphite)	$+ O_2(g)$	$= CO_2(g)$	-94100
C(graphite)	$+2\mathrm{H}_2(g)$	$= \mathrm{CH_4}(g)$	-14342

Example. For the reaction

$$H_2 + 1/2O_2 = H_2O(g)$$
,

we obtain from Table I the equations

$$(a) \ \ \mathbf{H}_2\mathbf{O}, \qquad C_{p} = 8 \cdot 81 - 0 \cdot 0019T + 0 \cdot 00000222T^2,$$

(b)
$$\mathbf{H}_2$$
, $C_p = 6.5 + 0.0009T$,

(c)
$$1/2O_2$$
, $C_p = 3\cdot25 + 0\cdot0005T$;

whence
$$\Delta C_p = (C_p)H_2O - \{(C_p)H_2 + (C_p)1/2O_2\}$$

is obtained by subtracting equations (b) and (c), for the reactants from (a), that of the resulting system. Thus we find that

$$\begin{split} \Delta C_p &= -0.94 - 0.0033T + 0.00000222T^2 \\ &= \frac{d\left(\Delta H\right)}{dT}. \end{split}$$

Integrating, we have

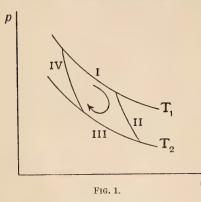
$$\Delta H = \Delta H_0 - 0.94T - \frac{0.0033T^2}{2} + \frac{0.00000222T^3}{3}.$$

The value of ΔH_0 is obtained by substitution if we know ΔH at any one value of T. When $T=273^\circ$ (absolute), ΔH has been found to be -57780 calories. Substituting these values we find that $\Delta H_0 = -57410$ calories.

Entropy. In the elementary theory we made use of certain criteria of chemical equilibrium which we obtained from a consideration of the Second Law of Thermodynamics. This law states that it is a characteristic of all spontaneous processes (i.e. changes which may occur of their own accord) that they can, if suitably carried out, be made to perform work. A system is in equilibrium if no spontaneous changes can, under any circumstances, occur in it, i.e. if none of the changes which might occur in it could be made to perform work. We therefore made use of the maximum work of a process as a measure of its tendency to occur. Now we have seen that the maximum work of a process is a definite quantity and independent of the way in which the reaction is carried out, provided every stage is reversible, only so long as the temperature remains constant. But if a system undergoes a change from a state A to a state Bat a different temperature the maximum work is no longer definite but depends on the path which is taken. The maximum work is thus in general not completely defined by the initial and final states of the system, and therefore we cannot construct a thermodynamic function which is related to the maximum work in just the same way as the energy is related to the energy changes of reactions. There is however a quantity, related to the maximum work, which like the energy change depends only on the initial and final states of the system, viz. the entropy change.

Consider a simple Carnot cycle, in which a quantity of matter, which is supposed to be always in a state of internal equilibrium, is put through a reversible cycle of operations (Fig. 1), consisting of two isothermal stages (I and III) at temperatures T_1 and T_2 ($T_1 > T_2$) respec-

tively and two connecting adiabatic stages (II and IV). Let the quantity of heat absorbed from surrounding



bodies in the isothermal stage I be q_1 and that absorbed in the isothermal stage III be q_2 (normally heat is evolved in the isothermal stage at the lower temperature T_2 ; q_2 is then a negative quantity). Then W, the work obtained in

the whole cycle, must be equal to the total amount of heat absorbed, *i.e.*

$$W = q_1 + q_2.$$

The ratio of the work obtained to the heat absorbed at the higher temperature, or W/q_1 , may be called the efficiency of the process.

Now Carnot's theorem states that all reversible cyclic processes working between the same two temperatures have the same efficiency. If this were not the case, as has been shown in Part I, it would be possible by the use of two such cyclic processes having different efficiencies and working one in the forward and one in the backward direction, to transfer heat from a colder to a hotter body (i.e. to reverse a spontaneous change) without the application of any outside effort. This is contrary to the Second Law of Thermodynamics.

The ratio W/q_1 is therefore the same for all reversible cycles working between the same two temperatures, and

is independent of the nature of the system employed as working substance. A scale of temperature may be defined in such a way that the efficiency is equal to the temperature difference between the two isothermal stages divided by the value of the temperature of the first isothermal stage, *i.e.* so that

$$\frac{W}{q_1} = \frac{T_1 - T_2}{T_1}$$
.(13)

This scale, the thermodynamic temperature scale devised by Lord Kelvin, is evidently quite independent of the nature of the substances used to establish it, and has therefore great advantages over a scale based on the thermal expansion of any actual substance. It agrees with the scale of temperature based upon the thermal expansion of a perfect gas.

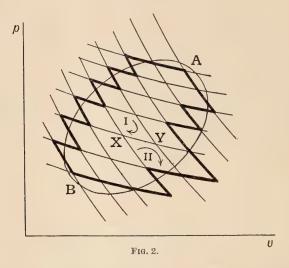
Substituting (12) in (13), we have

$$rac{q_1+q_2}{q_1}=rac{T_1-T_2}{T_1},$$
 or $rac{q_2}{q_1}=-rac{T_2}{T_1},$ $i.e.$ $rac{q_2}{T_2}+rac{q_1}{T_1}=0.$ (14)

Thus in a simple Carnot cycle the algebraic sum of the quantities of heat absorbed, each divided by the absolute temperatures at which the absorption takes place, is zero.

Now any reversible cycle whatever may be resolved into a number of elementary Carnot cycles. Consider a cyclic process tracing out the closed path AB on the p-v diagram (Fig. 2). We may resolve this cycle into a large number of simple Carnot cycles each having two isothermal and two adiabatic stages. On Fig. 2 are drawn some isothermal and adiabatic lines for the system

which form a number of Carnot cycles, the outside boundaries of which approximate roughly with the closed cycle AB. Every section of the isothermals which is not on the outside boundary is shared by two adjacent Carnot cycles. Thus the element XY is shared by the cycles I and II, and the quantities of work obtained in passing along the isothermal XY in the two cycles are



equal and opposite. The heat terms corresponding to the element XY also cancel out. It follows that all the heat and work terms corresponding to the shared sides balance out and we are left with only the terms for the outside boundary of the collection of Carnot's cycles. It is evident that by drawing the isothermals and adiabatics very close together we may make the outside boundaries of the Carnot cycles agree as closely as we wish with the actual boundary of our cycle AB.

For a single Carnot cycle we may write (14) as

$$\sum \frac{q}{T} = 0.$$

The same applies to a collection of Carnot cycles, and therefore to any reversible cyclic process, which as we have just seen can be resolved into a number of Carnot cycles. Therefore we may write for any reversible cyclic process

$$\sum \frac{q}{T} = 0, \dots (15)$$

the summation being taken right round the cycle.

Now if we have two states A and B of a system, at different temperatures, we may make a non-isothermal cycle by proceeding from A to B by a path I, and returning to the original state by a different path II (Fig. 3).

If every stage is carried out reversibly, we have by (15),

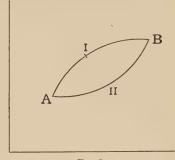


FIG. 3.

$$\sum \frac{q}{T_{(A \to B)_{\mathrm{I}}}} + \sum \frac{q}{T_{(B \to A)_{\mathrm{II}}}} = 0,$$

where the first term represents the sum of the q/T terms for the passage from A to B by path I, and the second term the same quantity for the passage from B to A by path II. Reversing the direction of the second term, we have

or
$$\begin{split} \sum \frac{q}{T_{(A \to B)_{\mathrm{I}}}} - \sum \frac{q}{T_{(A \to B)_{\mathrm{II}}}} = 0, \\ \sum \frac{q}{T_{(A \to B)_{\mathrm{I}}}} = \sum \frac{q}{T_{(A \to B)_{\mathrm{II}}}}. \end{split}$$

Thus, since we have placed no restriction on the path from A to B, except that it shall be reversible, the quan-

tity $\frac{q}{T_{(A \to B)}}$ must be a constant for all reversible paths

from A to B. This quantity thus depends only on the initial and final states A and B and not on the intermediate stages, and may be regarded as the difference between the values of a function of the state of the system in the two given states. This function is called the *entropy*. If S_A denotes the entropy of the system in the state A, and S_B that in the state B, the entropy change in going from A to B is

$$\Delta S = S_B - S_A = \sum \frac{q}{T_{(A \to B)}}, \dots (16)$$

the summation in the last term being taken over any reversible path between A and B.

It is important to notice that since the entropy change depends only on the initial and the final states of the system, it is the same however the change is conducted, whether reversibly or irreversibly. But it is only equal to

 $\sum \frac{q}{T}$ when the latter is evaluated for a reversible change.

As a consequence of this we can make a fundamental distinction between reversible and irreversible processes. Consider a change of a system from a state A to a state B. If carried out reversibly, the entropy change of the system is

 $\Delta S_{\mathrm{system}} = \sum \frac{q}{T}$.

Now all the heat absorbed by the system must come from some surrounding bodies, and it is a condition of reversibility that every element of heat absorbed must be taken from a body which has the same temperature as the system itself in this particular state. (The absorption of heat from bodies at other temperatures would necessarily introduce some irreversibility.) Therefore the entropy change of the surrounding bodies must be

$$\Delta S_{\rm surroundings} = -\sum \frac{q}{T},$$

since the surroundings give up the quantities of heat which are absorbed by the system and at the same temperatures. Thus for a reversible process

$$\Delta S_{\text{system}} + \Delta S_{\text{surroundings}} = 0, \dots (17)$$

i.e. in a reversible change the total entropy change of the system and its surroundings is zero.

On the other hand, in an irreversible change, the entropy change of the system in passing from the initial state A to the final state B is the same;

$$\Delta S_{\text{system}} = S_B - S_A$$
.

But this is no longer equal to $\Sigma q/T$ for the change. When a system undergoes an irreversible change, it performs less than the maximum amount of work, and since $q = \Delta E + w$, absorbs a smaller quantity of heat than in the corresponding reversible change. $\Sigma q/T$ is thus less in this case than in the reversible process. If the heat absorbed by the system at every stage comes from bodies at the same temperature, and the heat is transferred reversibly, the entropy decrease of the surroundings is $\Sigma q/T$.* Therefore the entropy decrease of the surround-

* The temperature of the bodies from which heat is absorbed by the system cannot be less than the temperature of the system, for heat will not pass from a body at a lower to a body at a higher temperature by itself. Hence the entropy decrease of the surroundings may be less than $\Sigma q/T$, but cannot be greater.

ings is less than the increase of entropy of the system, or

$$-\Delta S_{\text{surroundings}} < \Delta S_{\text{system}}$$
,

or
$$\Delta S_{\text{system}} + \Delta S_{\text{surroundings}} > 0.$$
(18)

To sum up, let us consider the system which undergoes change and the outside bodies, with which heat is exchanged, as one "system," which we may suppose to be entirely isolated from the action of any other bodies. We may state the following rules:

- when a reversible change occurs in any part of an isolated system, the total entropy remains unchanged;
- (2) when an irreversible change occurs in any part of an isolated system, the total entropy increases.

The Calculation of Entropy Changes. (1) Isothermal Changes. In order to find the entropy change of an isothermal process we need only carry out the process reversibly and divide the heat absorbed by the absolute temperature. For example, at the melting point of a solid, the solid and liquid forms of the substance are in equilibrium with each other, and the absorption of heat at constant pressure causes a change of the solid into liquid under reversible conditions. The entropy change in the fusion of a given mass of the solid is therefore

$$\Delta S = \frac{\Delta H}{T} \,, \quad \dots (19)$$

where ΔH is the heat absorbed, *i.e.* the latent heat of fusion of the given mass of the solid, and T the absolute temperature at which the fusion takes place. The entropy change in vaporisation in similarly obtained.

Examples.

1. The latent heat of fusion of water at its melting point under a pressure of 1 atmosphere (273° K.) is 1438 calories per gram molecule. The entropy change is therefore

$$\Delta S = \frac{1438}{273 \cdot 1} = 5.27$$
 calories/degrees.

2. The latent heat of vaporisation of water at 373·1° K. (1 atmosphere pressure) is 9730 calories per gram molecule. The entropy change is therefore

$$\Delta S = \frac{9730}{373 \cdot 1} = 26.5$$
 calories/degrees.

This is the difference between the entropy of a gram molecule (18 grams) of water vapour at 1 atmosphere pressure and 373·1° K. and that of liquid water at the same temperature.

In the isothermal expansion of a perfect gas, the energy change is zero and the heat absorbed is equal to the work performed by the gas. For a reversible expansion of a gram molecule of the gas from a pressure p_1 to a pressure p_2 , the heat absorbed is thus

$$q = w = RT \log p_1/p_2.$$

The entropy change is thus

$$\Delta S = q/T = R \log p_1/p_2. \quad \dots (20)$$

It should be observed that the entropy change of the gas has this value whether the expansion is conducted reversibly or not (but it can only be calculated from the heat absorbed in the reversible process). In an irreversible expansion the work done by the gas, and the heat absorbed from the surroundings is less than that given above. The entropy decrease of the surroundings is therefore less than the increase in the entropy of the gas.

Consequently when a gas expands irreversibly there is an increase in the total entropy of the gas and its surroundings.

(2) Non-isothermal Changes. To find the entropy change of a reversible non-isothermal process, we must sum the quantities of heat absorbed, each divided by the absolute temperature at which the absorption takes place. It is always possible to add heat reversibly to a body, thereby increasing its temperature, if the body is placed in contact with sources of heat which have a temperature only infinitesimally higher than that of the body itself. Under these circumstances the absorption of heat takes place very slowly and the body remains in a state of thermal equilibrium (uniform temperature) throughout. The heat absorbed in raising the temperature of a body from T to T+dT, at constant pressure, is $dH=C_pdT$, and the entropy change is therefore

$$dS = \frac{dH}{T} = \frac{C_p}{T} \cdot dT. \quad \dots (21)$$

To find the entropy change in a finite change of temperature from T_1 to T_2 , we must integrate this expression between the given temperature limits, *i.e.*

$$\Delta S_{T_1}^{T_2} = \int_{T_1}^{T_2} \frac{C_p}{T} \cdot dT. \qquad (22)$$

Examples.

1. The molar heat capacity of helium (a monatomic gas) between -200° C. and 0° C. is $5\cdot0$. The entropy change between these temperatures is therefore

$$\begin{split} \Delta S_{73}^{273} = & \int_{73}^{273} \frac{5}{T} \cdot dT = \int_{73}^{273} 5 \cdot d \log T \\ = & 5 \log_e \frac{273}{73} = 6 \cdot 61 \text{ calories/degrees.} \end{split}$$

2. The molar heat capacity of liquid mercury between -40° C. and $+140^{\circ}$ C. is given by the equation

$$C_p = 8.42 - 0.0098T + 0.0000132T^2$$
.

The entropy change between these temperatures is thus

$$\begin{split} \Delta S_{233}^{413} = & \int_{233}^{413} \left(\frac{8 \cdot 42 - 0 \cdot 0098T + 0 \cdot 0000132T^2}{T} \right) dT \\ = & 8 \cdot 42 \log_e \left(\frac{413}{233} \right) - 0 \cdot 0098 \left(413 - 233 \right) \\ & + \frac{0 \cdot 0000132}{2} \left(413^2 - 233^2 \right) \end{split}$$

=4.82-1.76+1.54=4.60 calories/degrees.

Criteria of Equilibrium. Irreversible changes can only occur in a system of bodies which is not in a state of equilibrium. When equilibrium is established no irreversible changes are possible and consequently, when the absorption of heat from outside bodies is excluded, there are no possible changes whereby the entropy can increase. Thus when an isolated system of bodies, the energy of which is constant, is in equilibrium, its entropy has a maximum value. Regarding the universe as an isolated system, Clausius therefore summed up the generalisation of natural tendencies which is contained in the Second Law of Thermodynamics by the statement—"The entropy of the universe tends to a maximum."

We have here also a very valuable criterion of chemical equilibrium. A system is in equilibrium if no variations in its state can occur spontaneously. If there is any variation in its state (which does not alter its energy) which causes an increase of entropy, the system cannot be in equilibrium, for this variation may occur spontaneously. (It does not follow that it will occur.) Gibbs therefore gave the following proposition as a general criterion of equilibrium:

R

GIBBS' FIRST CRITERION.

For the equilibrium of any isolated system it is necessary and sufficient that in all possible variations in the state of the system which do not alter its energy, the variation of the entropy shall either vanish or be negative.

In using this criterion we need generally only consider infinitesimally small variations, for an infinitesimally small variation must necessarily precede a finite one, and if the former cannot occur neither can the latter. The criterion can therefore be written in the form:

$$(\delta S)_E \leq 0, \dots (23)$$

 $(\delta S)_E$ denotes the variation of the entropy in an infinitesimal variation of the state of the system, for which the energy remains constant.

The criterion can be expressed in an alternative form which is more convenient for practical use. Consider some particular state of a system (not necessarily a state of equilibrium). If there is another state which has less energy but the same entropy, we can by adding heat, arrive at a state which has the same energy and more entropy than the original state, *i.e.* if there is a state with less energy and the same entropy, there is also a state with more entropy and the same energy. But if this is the case the original state cannot be a state of equilibrium. It is therefore a characteristic of a state of equilibrium that the energy is a minimum for constant entropy. This is stated in the following proposition of Gibbs:

GIBBS' SECOND CRITERION.

For the equilibrium of any isolated system it is necessary and sufficient that in all possible variations in the state of the system which do not alter its entropy, the variation of its energy shall either vanish or be positive.

For the same reasons as those given in connection with the first criterion, we may express this condition as follows: $(\delta E)_S \ge 0, \dots (24)$

 $(\delta E)_S$ denotes the variation of the energy in an infinitesimal variation, for which the entropy remains constant.

The Variation of the Energy. In order to apply this last criterion we need to know how the energy of the system under consideration and of the bodies composing it varies in the different variations of which they are capable. The energy of a body may be varied in three ways, (1) by the absorption of heat, (2) by performing work on its surroundings, (3) by a change in its amount or composition. With changes of the last kind we shall be principally concerned in the succeeding chapters of this book. For the present we will consider a body having a constant composition, a uniform temperature T and uniform pressure p. Suppose that this body absorbs a small quantity of heat dq and increases in volume by a small amount dv. The increase in its energy, by (2), is

$$dE = dq + p dv,$$

but since the increase in entropy is dS = dq/T, we may write, for an infinitesimal change

$$dE = T dS + p dv. \qquad \dots (25)$$

*As an illustration of the use of (24), we will find the conditions necessary for thermal and mechanical equilibrium in a heterogeneous system. Suppose that the system is contained in a rigid envelope of constant volume which is supposed to be impermeable to heat. This ensures that (1) the total volume of the system remains constant, and (2) since if the system is in equilibrium its entropy cannot be in-

creased except by the absorption of heat, its total entropy remains constant. Suppose that the whole mass enclosed in this envelope is divided into a number of parts C', C'', etc., each of which is perfectly homogeneous. Let E', S', V', P' and T' be the energy, entropy, volume, pressure and temperature of the part C'; E'', S'', V'', P'', T'', the same quantities for the part C'', and so on. The variation of the energy of the part C', when it receives heat from other parts of the system or changes its volume, by (25) is

$$\delta E' = T'\delta S' + P'\delta V', * \dots (26)$$

Similarly for the other parts, we have

$$\delta E^{\prime\prime} = T^{\prime\prime} \delta S^{\prime\prime} + P^{\prime\prime} \delta V^{\prime\prime},$$

$$\delta E^{\prime\prime\prime} = T^{\prime\prime\prime} \delta S^{\prime\prime\prime} + P^{\prime\prime\prime} \delta V^{\prime\prime\prime}, \text{ etc.} \dots (27)$$

The condition $(\delta E)_S \ge 0$, means that for equilibrium it is necessary that

$$\delta E' + \delta E'' + \delta E''' + \text{etc.} \ge 0, \dots (28)$$

for all possible variations in the state of the system which do not alter its entropy, *i.e.* introducing the values given in (26) and (27),

$$T'\delta S' + T''\delta S'' + T'''\delta S''' \dots$$

+ $P'\delta V' + P'''\delta V'' + P'''\delta V''' \dots \ge 0, \dots (29)$

for all possible variations in which the total entropy remains constant, i.e. for which

$$\delta S' + \delta S''' + \delta S'''' + \dots = 0.$$
(30)

Since the total volume of the system is also kept constant by the rigid envelope, the possible variations only include those for which

$$\delta V' + \delta V'' + \delta V''' \dots = 0$$
.(31)

* Changes of the composition of the different parts, by the transfer of substances from one part to another, are excluded here.

(29) must hold, when $\delta S'$, $\delta V'$, $\delta S''$, $\delta V''$, etc., have any values, positive or negative, provided (30) and (31) are satisfied. The reader can easily satisfy himself * that (29) cannot hold under these conditions unless

$$T' = T'' = T''' = \text{etc.}$$
(32)

$$P' = P'' = P''' = \text{etc.}$$
(33)

Therefore it is necessary for equilibrium that all parts of the system shall be at the same temperature and pressure,

It is assumed here, of course, that the system is so small that the effect of gravitation need not be considered, *i.e.* that no appreciable work is performed against gravitational forces if any part of the system changes its position.

The Functions A and F. We have already given two quite general criteria of chemical equilibrium. In practice we meet very frequently with cases of equilibrium for which it is a condition that the temperature or the temperature and pressure remain constant. The treatment of such problems is facilitated by the use of two other functions which we shall now discuss.

These functions are defined by the equations

$$A = E - TS$$
,(34)

$$F = E - TS + pv = H - TS$$
.(35)

All these quantities have definite values in every state of a system, so that A and F are thermodynamic functions of the state of the system.

In order to show the significance of these quantities, consider first a change of state of a system from a state I

* Consider a variation in which only S' and S'' vary. Then by (30), $\delta S' + \delta S'' = 0$, or $\delta S' = -\delta S''$. Thus (29) becomes $(T' - T'')\delta S' \ge 0$, and this cannot hold for positive and negative values of $\delta S'$, unless T' = T''.



to a state II which are both at the same temperature T. The change in A is

$$\Delta A = A_{II} - A_{I}$$

$$= (E_{II} - TS_{II}) - (E_{I} - TS_{I})$$

$$= E_{II} - E_{I} - T(S_{II} - S_{I})$$

$$= \Delta E - T\Delta S.$$
(36)

Now if the change be carried out reversibly $T\Delta S$ is equal to the heat absorbed q, and $\Delta E - q$ is by (2) equal to -w, *i.e.*

$$\Delta A = -w, \dots (37)$$

where w is the maximum work of the change. The increase in A, in a change at constant temperature, is thus equal to the work performed on the system in carrying out the change reversibly. Similarly a decrease in A is equal to the maximum work performed by the system.

The maximum work of a change is, as we have seen, a definite quantity only so long as the temperature remains constant throughout. But in A we have a function which has a definite value for every state of a system without restriction, which is such that the change in its value reduces, for a constant temperature process, to the maximum work. A can thus be regarded as the maximum work function.

We have used the maximum work as a criterion of equilibrium for systems which are maintained at constant temperature. A system is in equilibrium at constant temperature if there is no process whereby it could perform work, *i.e.* no process whereby the function A might be decreased. We can thus write as the criterion of equilibrium at constant temperature:

$$(\delta A)_T \geq 0, \ldots (38)$$

i.e. in all possible variations in the state of a system, while the temperature remains constant, the variation of the maximum work function A shall either vanish or be positive.

Secondly, consider a change of state of a system from a state I to a state II, which are both at the same temperature T and pressure p. The change in F is

$$\Delta F = F_{II} - F_{I}$$

$$= (E_{II} - TS_{II} + pv_{II}) - (E_{I} - TS_{I} + pv_{I})$$

$$= \Delta E - T\Delta S + p\Delta v. \qquad (39)$$

As in the previous case, $T\Delta S$ is the heat absorbed when the change is carried out reversibly, so that

$$\Delta F = -(w - p\Delta v) = -w', \qquad \dots (40)$$

for $p\Delta v$ is the work done against the constant pressure pin the volume change Δv , and $w - p\Delta v$ is equal to the net work of the change w'. The increase in F for a change at constant temperature and pressure is thus equal to the net work performed on the system in carrying out the change reversibly. The decrease of F in such a change is similarly equal to the net work performed by the system. F can therefore be regarded as the net work function. It is known as the free energy. F itself has a definite value for every state of a system without restriction. But for changes at constant temperature and pressure, the change in F becomes equal to the net work performed on the system.

A system is in internal equilibrium at constant temperature and pressure if there is no change whereby net work could be obtained, i.e. if no process can occur in it whereby the value of F is decreased. We can therefore write as the criterion of equilibrium at constant temperature and pressure:

 $(\delta F)_{T,n} = 0, \dots (41)$

i.e. in all possible variations in the state of a system, which do not alter its temperature and pressure, the variation of the free energy F shall either vanish or be positive.

The functions H, A and F were first employed by J. W. Gibbs in his monumental papers on the application of thermodynamics to material systems.*

The notation used in this volume is that of Lewis and Randall,† but it will be of assistance to those who refer to the original papers of Gibbs to give his symbols.

Lewis and Randall.	Gibbs.	Name.
E	ϵ	Energy.
S	η	Entropy.
H	χ	Heat function for constant pres-
		sure (G.) or Heat content (L.
		and R.).
A	ψ	Available energy.
F	5	Free energy (L. and R.).

A certain amount of confusion has arisen in the literature because Helmholtz used the term free energy for A. Massieu, in 1869, was the first to use functions like A and F, and to demonstrate their usefulness. The functions he used, in our notation, were

$$\frac{-E+TS}{T}$$
 or $-\frac{A}{T}$ and $\frac{-E+TS-pv}{T}$ or $-\frac{F}{T}$.

Planck has also made use of the latter function, which has the same properties in a system at constant temperature and pressure as the entropy at constant energy and volume.

^{*} Scientific Papers, vol. i. (Longmans Green).

[†] Thermodynamics and the Free Energy of Chemical Substances (1923).

Variation of the Functions A and F with Temperature and Pressure. If we differentiate F (equation 35) in the most general way, we obtain

$$dF = dE - T dS - S dT + p dv + v dp,$$

but by (25), dE - TdS + pdv = 0, so that we have

$$dF = -S dT + v dp. \quad \dots (42)$$

Therefore when the pressure is constant (dp = 0), we have

$$\left(\frac{dF}{dT}\right)_p = -S, \quad \dots (43)$$

and for constant temperature (dT=0);

$$\left(\frac{dF}{dp}\right)_T = v.$$
(44)

It obviously follows that since $F_2 - F_1 = \Delta F$,

$$\left(\frac{d(\Delta F)}{dT}\right)_{p} = -(S_{2} - S_{1}) = -\Delta S. \qquad (45)$$

and

Now, by (35), $\Delta F = \Delta H - T \Delta S$,

and substituting the value of ΔS given by (45) in this equation, we have

$$\Delta F - \Delta H = T \left(\frac{d(\Delta F)}{dT} \right)_{p}$$
 (47)

This equation will be familiar as the Gibbs-Helmholtz equation. It can be written in another form, which is sometimes convenient in practice. Differentiating the quotient $\Delta F/T$, we have

$$\frac{d(\Delta F)/T}{dT} = \frac{1}{T} \left(\frac{d(\Delta F)}{dT} \right) - \frac{\Delta F}{T^2} \,.$$

Comparing this with (47), we see that

$$\left(\frac{d(\Delta F/T)}{dT}\right)_{p} = -\frac{\Delta H}{T^{2}}.$$
 (48)

It can easily be shown by similar methods that

$$\left(\frac{d(F/T)}{dT}\right)_{p} = -\frac{H}{T^{2}}, \dots (49)$$

i.e. the rate of variation of (F/T) with the temperature, at constant pressure is equal to minus the heat content divided by the square of the absolute temperature.

Again, if we differentiate A (equation 34), we obtain dA = dE - TdS - SdT.

Therefore, substituting (25), we have

$$dA = -S dT + p dv. \dots (50)$$

Therefore we have

$$\left(\frac{dA}{dT}\right)_v = -S, \quad \dots \tag{51}$$

and

$$\left(\frac{dA}{dv}\right)_T = p. \tag{52}$$

Substituting in A = E - TS, the value of S given by (51), we have:

$$A - E = T \left(\frac{dA}{dT}\right)_{v}, \qquad (53)$$

from which it is easy to obtain the equation

$$\left(\frac{d(A/T)}{dT}\right)_v = -\frac{E}{T^2}.$$
 (54)

Similar equations can of course be written for ΔA and ΔE .

Equilibrium of Two Phases of a Single Substance. As a simple illustration of the use of the free energy, we will consider the equilibrium of two phases, e.g. solid and liquid, or liquid and vapour, of a single substance. We have already seen that it is necessary for equilibrium that

the pressure and the temperature shall be the same in the two phases. We will suppose that the two phases are in contact with each other and are maintained at a constant temperature and pressure. The criterion of equilibrium (41) is that in all possible variations of the system under these conditions the variation of the free energy shall either vanish or be positive. Let F' and F'' be the free energies of a gram molecule of the substance in the two phases. Consider a variation, viz. the transfer of a small quantity dn gram molecules of the substance from the first phase to the second. The decrease of the free energy of the first phase is F'dn and the increase in the free energy resulting from the transfer is thus

$$\delta F = F''dn - F'dn = (F'' - F')dn.$$

If the phases are in equilibrium this quantity must either be zero or negative for all possible variations, *i.e.* for all possible values of dn. Since dn may be either positive or negative, it is obvious that this requirement can only be fulfilled if F'' = F', *i.e.* for equilibrium the free energy of the same mass of the substance must be the same in both phases. Thus water and ice can be in equilibrium when the free energies of equal quantities of water and ice are the same.

Suppose that we have equal quantities of the two phases in equilibrium with each other. Let the temperature and pressure be slightly varied in such a way that the equilibrium is still maintained. In the varied state the free energies of the two phases must still be equal, and therefore the change of free energy of the two phases must be the same. The variation of the free energy of the first phase, by (42), is

$$dF' = -S'dT + v'dp,$$

or

and that of the second phase,

$$dF'' = -S''dT + v'dp.$$

Since dF' = dF'', we have

$$-S'dT + v'dp = -S''dT + v''dp, \frac{dT}{dp} = \frac{v'' - v'}{S'' - S'}.$$
 (55)

S'' - S', the difference of entropy of the two phases, is equal to q/T, where q is the heat absorbed in changing the given mass from the first state to the second state.

Therefore,

$$\frac{dT}{dp} = \frac{(v'' - v')T}{q}, \dots (56)$$

which is Clausius's equation.

Examples.

1. Using the heat capacity data in Table I, formulate equations for the variation with the temperature of the heat content changes in the reactions:

$$\begin{aligned} 1/2 N_2 + 3/2 H_2 = & NH_3 \ ; \\ & CO_2 + H_2 = & CO + H_2O \ ; \\ 1/2 H_2 + 1/2 Br_2 = & HBr. \end{aligned}$$

*2. The heat capacities of rhombic and monoclinic sulphur are given by the equations,

$$S_r$$
, $C_p = 4.12 + 0.0047T$; S_m , $C_p = 3.62 + 0.0072T$.

The heat content change in the reaction $S_r = S_m$ is 77.0 cals. at 0° C.

Deduce expressions for (1) the variation of the heat content change with the temperature, (2) using (48), the variation of the free energy change with the temperature. The transition point is 95.0° C.

$$(\Delta F = 120 + 0.50T \log T - 0.00125T^2 - 2.82T.)$$

3. Using Table I, find the entropy change of H_2 between 0° C. and 200° C., at constant pressure. (5.72 cals °.)

CHAPTER II

THE THERMODYNAMICS OF PERFECT GAS REACTIONS

The Free Energy of Perfect Gases. By (20) the entropy change when a gram molecule of a perfect gas is expanded at constant temperature from unit pressure to a pressure p is $\Delta S = R \log 1/p = -R \log p$,

If S° is its entropy at unit pressure, and S its entropy at the same temperature at the pressure p, we have therefore

$$S = S^{\circ} - R \log p. \dots (57)$$

The free energy, by (35), is

$$F = E - TS + pv,$$

and introducing this value of S, we have

$$F = E - TS^{\circ} + pv + RT \log p.$$
(58)

Since the energy and the product pv(=RT) for a perfect gas are not altered by a change of pressure at constant temperature, $E-TS^{\circ}+pv$ is the free energy of the gas at the temperature T and unit pressure. If we denote this quantity by F° , we have

$$F = F^{\circ} + RT \log p. \quad \dots (59)$$

Similarly it is easy to show that

$$A = A^{\circ} + RT \log p, \dots (60)$$

where A° is the value of A for a gram molecule of the gas at the temperature T and unit pressure, and evidently

$$F^{\circ} = A^{\circ} + RT$$
.(61)

A perfect gas mixture is one for which the total pressure is equal to the sum of the pressures which each constituent would exert if present by itself in the same space. Or since the total pressure may be regarded as the sum of the partial pressures of the different constituents, we may define a perfect gas mixture as one for which the partial pressure of each constituent is equal to the pressure it would exert if it occupied the same space alone, i.e. the partial pressure of each constituent is unaffected by the presence of the others. It follows that the free energy of a perfect gas mixture may be regarded as the sum of the free energies of the various constituents, each of which is equal to the free energy which this constituent would have if it occupied the same space by itself. Suppose that we have a perfect gas mixture at the temperature T, containing the substances A, B, C, D, at the partial pressures p_A , p_B , p_C , p_D . The free energies, per gram molecule, of these substances in the mixture are

$$F_{A} = F^{\circ}_{A} + RT \log p_{A},$$

$$F_{B} = F^{\circ}_{B} + RT \log p_{B},$$

$$F_{C} = F^{\circ}_{C} + RT \log p_{C},$$

$$F_{D} = F^{\circ}_{D} + RT \log p_{D},$$

$$(62)$$

where F_A° , F_B° , F_C° , F_D° , are the free energies of the respective gases at the temperature T and at unit pressure.

Equilibrium in Perfect Gas Mixtures. Consider a perfect gas mixture containing the four substances A, B, C, and D, and suppose that C and D can be formed from

A and B, or vice versa, in accordance with the chemical equation:

$$aA + bB = cC + dD$$
.(63)

(In this equation A, B, C, and D represent the chemical symbols of these substances or, quantitatively, the gram molecule of the respective substances. The equation thus represents the *amounts* of the substances entering into the reaction.) Suppose further that the mixture is in equilibrium at a total pressure P and temperature T, and that the partial pressures of the constituents are p^e_A , p^e_B , p^e_C , p^e_D . In order to discover the relation between the partial pressures in the equilibrium mixture, we can use the criterion (41), viz.

$$(\delta F)_{PT} \geq 0, \dots (64)$$

i.e. all the possible variations in the state of the mixture, so long as its temperature and pressure remain unaltered, must either increase the free energy or leave it unchanged. None can decrease it.

We will suppose then that the temperature and pressure are kept constant. The state of the mixture may be varied by the change of A and B into C and D or vice versa, in accordance with (68). Suppose that the increases in the amounts of A, B, C and D in any small variation are dn_A , dn_B , dn_C , dn_D (gram molecules), then if F_A , F_B , F_C , F_D , are the free energies per gram molecule in the mixture, the change of the free energy in the supposed variation is

$$F_A dn_A + F_B dn_B + F_C dn_C + F_D dn_D.$$

This quantity must be greater than or equal to zero for all possible variations. The amounts of the substances which disappear, or are formed in the reaction must be in accordance with the chemical equation. If C and D are formed from A and B, dn_C and dn_D are positive and dn_A and dn_B negative and their values must be proportional to c, d and -a, -b respectively, i.e.

$$dn_A:dn_B:dn_C:dn_D::-a:-b:c:d.$$

We can therefore write (64) as

$$-aF_A - bF_B + cF_C + dF_D \ge 0$$
.....(65)

If the supposed variation is in the reverse direction, A and B being formed from C and D, dn_A and dn_B are positive and dn_C and dn_D negative, and

$$dn_A : dn_B : dn_C : dn_D : : a : b : -c : -d.$$

For this variation, we have

$$aF_A + bF_B - cF_C - dF_D \ge 0.$$
(66)

But (65) and (66) cannot both hold except when the equality holds in each case,

i.e.
$$-aF_A - bF_B + cF_C + dF_D = 0$$
,(67)

If we now substitute for F_A , F_B , etc., the values given by (62), we have

$$\begin{aligned} -aF^{\circ}_{A} - bF^{\circ}_{B} + cF^{\circ}_{C} + dF^{\circ}_{D} - aRT \log p^{e}_{A} \\ -bRT \log p^{e}_{B} + cRT \log p^{e}_{C} + dRT \log p^{e}_{D} = 0. \end{aligned}$$

Now $cF^{\circ}_{C} + dF^{\circ}_{D} - aF^{\circ}_{A} - bF^{\circ}_{B}$ is the difference between the free energy of c mols of C and d mols of D at unit pressure and that of a mols of A and b mols of B also at unit pressure, *i.e.* the free energy change in the reaction when we start with the reactants at unit pressure and finish with the gases formed also at unit pressure. Denoting this quantity by ΔF° , we have

$$\Delta F^{\circ} + RT(c \log p^{e_C} + d \log p^{e_D} - a \log p^{e_A} - b \log p^{e_B}) = 0. \dots (68)$$

The quantity within the brackets can be recognised as the logarithm of the equilibrium constant K_p , where

$$K_p = (p_C)^c (p_D)^d / (p_A)^a (p_B)^b, \dots (69)$$

so that

$$\Delta F^{\circ} = -RT \log_{e} K_{p}. \qquad \dots (70)$$

Change of Equilibrium Constant with Temperature. By (48), we have

$$\left(\frac{d(\Delta F^{\circ}/T)}{dT}\right)_{P} = -\frac{\Delta H^{\circ}}{T^{2}}, \quad(71)$$

where ΔH° is the change of heat content corresponding to ΔF° , *i.e.* for the change of the reactants at unit pressure into the resultants at unit pressure. Introducing the value $\Delta F^{\circ} = -RT \log K_{v}$, we have

$$\frac{d(\log K_{p})}{dT} = \frac{\Delta H^{\circ}}{RT^{2}}. \quad \dots (72)$$

We have already seen (Part I, p. 95) how this equation can be integrated over a limited range of temperature over which ΔH° can be regarded as constant. It can be integrated over a wide range of temperature if the variation of ΔH° with the temperature is known. When equations similar to those in Table II are known for the heat capacities of the gases concerned, the heat content change in the reaction can be formulated as in (12) by a series of the form

$$\Delta H = \Delta H_0 + \alpha' T + \beta' T^2 + \gamma' T^3 + \delta' T^4 \dots, \dots (73)$$

where ΔH_0 is the value of ΔH as determined by this equation when T=0. (The heat content of a perfect gas does not vary with its pressure, so that ΔH° , the value for unit pressure, is the same as that determined for any convenient pressure. For actual gases at moderate

pressures the distinction between ΔH (the heat content change for any given pressure) and ΔH° can be neglected.)

Introducing this value of ΔH into (72), we have

$$\frac{d(\log_{\mathrm{e}}K_{\mathrm{p}})}{dT} = \frac{\Delta H_{\mathrm{0}}}{RT^{2}} + \frac{\alpha'}{RT} + \frac{\beta'}{R} + \frac{\gamma'T}{R} + \frac{\delta'T^{2}}{R} + \cdots \; , \label{eq:delta_p}$$

and integrating this:

$$\begin{split} \log_{\mathfrak{s}} & K_{\mathfrak{p}} = -\frac{\Delta H_{0}}{RT} + \frac{\alpha'}{R} \log T + \frac{\beta'T}{R} + \frac{\gamma'T^{2}}{2R} + \frac{\delta'T^{3}}{3R} \\ & + \ldots + J, \quad (74) \end{split}$$

where J is an integration constant. J can be evaluated when the value of K_p for one value of T is known. Since $\Delta F^{\circ} = -RT \log K_p$, we obtained by multiplying (74) through by -RT:

$$\Delta F^{\circ} = \Delta H_0 - \alpha' T \log T - \beta' T^2 - \frac{\gamma'}{2} T^3 - \frac{\delta'}{3} T^4 \dots - IT$$
 (75) where $I = JR$.

This equation gives the variation of the free energy change with the temperature over the same range of temperature as that to which the heat capacity equations apply.

Examples.

1. We found (p. 6) that the heat content change in the reaction

$$H_2 + 1/2O_2 = H_2O(g)$$
(a)

can be represented for a range of temperature from 0° C. to over 1000° C. by the equation

$$\Delta H = -57410 - 0.94T - 0.00165T^2 + 0.00000074T^3.$$

Inserting this value into $(d \log K_p/dT) = \Delta H/RT^2$ and integrating, we have

$$\begin{split} \log K_{p} = & \frac{57410}{RT} - \frac{0.94}{R} \log T - \frac{0.00165T}{R} \\ & + \frac{0.00000074T^{2}}{2R} ... + J, \end{split}$$

where J is the integration constant.

In order to evaluate J we may make use of Nernst and von Wortenberg's measurements of the dissociation of water vapour. They found that at 1480° K. the percentage dissociation of water vapour is 0.0184. The equilibrium constant at this temperature is thus

$$K_p = \frac{p_{H_2O}}{p_{H_2} \cdot p_{O_2}^{-1/2}} = \frac{1}{0.000184 \times (0.000092)^{1/2}} = 5.66 \times 10^5.$$

Introducing this figure, and the value of T into the equation, we find that J = -1.98. Similarly

$$\begin{split} \Delta F^\circ &= -RT \log \, K_{\,p} \\ &= -57410 + 0.94 \log \, T + 0.00165 T^2 \\ &\quad + 0.00000037 T^3 + 3.94 T, \end{split}$$

where 3.94 = -JR. By means of this equation we can find ΔF° at any other temperature. Thus when $T = 298(25^{\circ} \text{ C.})$, we have

$$\Delta F^{\circ}_{298} = -54590$$
 calories.

After an examination of all the available data for the free energy of formation of water vapour Lewis and Randall have given 3.92 as the best value of I.

2. It is of interest to calculate from this result the theoretical electromotive force of the reversible oxygenhydrogen cell at 25° C.

The reaction

$$H_2(g) + 1/2O_2(g) = H_2O(l), \dots (b)$$

differs from that considered above in that the water formed is obtained as liquid water. To obtain ΔF for this reaction, we must add to ΔF° (the free energy change for gases at unit pressure), the free energy change in the change of water vapour at unit pressure (and 25°) to liquid water at the same temperature. The vapour pressure of liquid water at 25° is 23.8 mm. of mercury. Water vapour at this pressure must have the same free energy (per mol) as liquid water, so that we need only evaluate the free energy change in the isothermal expansion of water vapour from unit pressure (1 atmosphere) to a pressure of 23.8 mm. By (59) we have therefore

$$\Delta F_{\rm 298}(g\rightarrow l) = RT \, \log \frac{23 \cdot 8}{760} = -2053 \, \, {\rm calories.} \label{eq:fitting}$$

The total free energy change for the reaction (2) is therefore

 $\Delta F_{298} = -54590 - 2050 = -56640$ calories.

Two Faradays of electricity must pass through the oxygen-hydrogen cell in order to bring about the reaction represented by (b). Therefore if E is the reversible electromotive force

 $2EF = 56640 \times 4.182 \text{ joules,}$

or $E = \frac{56640 \times 4.182}{2 \times 96490} = 1.227 \text{ volts.}$

3. From the heat capacity equations we can derive the equation

$$\Delta H = \Delta H_0 - 4.96T - 0.0006T^2 + 0.0000017T^3,$$

for the heat content change in the reaction

$$1/2N_2(g) + 3/2H_2(g) = NH_3(g)$$
.

(See Chapter I, ex. 1.) By the use of thermochemical data it is found that $\Delta H_0 = -9500$ calories. Introducing this value of ΔH into (72), and integrating, we have

$$\begin{split} \log K_p = & \frac{9500}{RT} - \frac{4\cdot96}{R} \log T - \frac{0\cdot000575T}{R} + \frac{0\cdot0000017T^2}{2R} + J, \\ \text{and} \quad & \Delta F^\circ = -RT \log K_p \end{split}$$

$$egin{array}{l} \Delta F^* &= -KT \log \mathbf{K}_p \\ &= -9500 + 4.96T \log T + 0.000575T^2 \\ &- 0.00000085T^3 + IT, \end{array}$$

From measurements of the equilibrium constant at various temperatures and pressures, Lewis and Randall conclude that the best value of I is -9.61.

The Vapour Pressure Equation. The equilibrium between a solid or liquid and its vapour can be similarly treated. Let F_s be the molar free energy of a solid at

the temperature T, and F_g that of the vapour. For equilibrium it is necessary that $F_s = F_g$. If F_g° is the free energy of the vapour at this temperature, and at unit pressure, and p the vapour pressure, we have by (59), assuming that the vapour is a perfect gas,

$$F_g = F_g^{\circ} + RT \log p,$$

$$F_s - F_a^{\circ} = RT \log p. \qquad (76)$$

and therefore

Therefore, by (48),

$$\begin{split} \frac{d \log p}{dT} &= \frac{1}{R} \left(\frac{d(F_s/T)}{dT} - \frac{d(F_g^{\circ}/T)}{dT} \right) \\ &= -\frac{H_s - H_g^{\circ}}{RT^2} = \frac{\Delta H_s}{RT^2}, \dots (77) \end{split}$$

where $\Delta H = H_g^{\circ} - H_s$ is the latent heat of vaporisation.

The dissociation equilibrium between solids and a gas can be similarly treated. Consider the reaction

$$\mathrm{CaCO_3} = \mathrm{CaO} + \mathrm{CO_2}.$$

It can easily be shown by the method previously used that the condition of equilibrium is

$$F_{CaCO_3}\!=\!F_{CaO}+F_{CO_2},$$

where F_{CaCO_3} , F_{CaO} , F_{CO_2} , are the free energies at a given temperature of the quantities of these substances which are represented in the chemical equation. Writing $F_{CO_2} = F^{\circ}_{CO_2} + RT \log p$, we thus have for equilibrium:

$$F_{CaCO_3} - F_{CaO} - F^{\circ}_{CO_2} = \Delta F^{\circ} = RT \log p,$$

and by the same method as above

$$\frac{d \log p}{dT} = \frac{\Delta H}{RT^2},$$

where ΔH is the heat content change in the reaction.

These expressions can be integrated similarly to (72), if ΔH is known as a function of T.

Examples.

1. The heat capacity change in the reaction

$$SO_2(g) + 1/2O_2 = SO_3(g)$$

can probably be taken as zero. The heat content change is thus independent of the temperature, and was found by Berthelot to be $\Delta H = -22600$. Formulate an expression giving $\log K_p$ as a function of the temperature. Given $\log_{10} K_p = 0.268$ at 1000° K. the integration constant of this expression can be evaluated, hence ΔF° can be expressed as a function of the temperature.

$$(\Delta F^{\circ} = -22600 + 21.37T.)$$

2. For the water-gas reaction:

$$CO_2(g) + H_2(g) = CO(g) + H_2O(g),$$

take the heat content equation from Chapter I, ex. l, and write down an expression for the equilibrium constant. The integration constant can be evaluated by inserting the value $K_p = 0.840$ at 1059° K. Formulate the expression for ΔF° .

$$(\Delta F^{\circ} = 10100 - 1.81T \log T + 0.00445T^{2} - 0.00000068T^{3} - 0.54T.)$$

3. The free energy change in the reaction

$$N_2(g) + O_2(g) = NO(g)$$

is expressed by $\Delta F^{\circ} = 21600 - 2.50T$. Find the equilibrium constant when

$$T = 1000$$
 and $T = 2000$. $(6.8 \times 10^{-5}, 1.5 \times 10^{-2})$

4. Write down an expression for ΔF° for the reaction

$$1/2H_2(g) + 1/2Br_2(g) = HBr(g)$$
.

Use the heat capacity equations of Table I. and the values

$$\Delta H_0 = -11970 \; ; \; \log_{l\delta} K_p = 2 \cdot 44 \; \text{ when } \; T = 1381^\circ \; \mathrm{K}.$$

$$(\Delta F^\circ = -11970 + 0 \cdot 45T \; \log \; T - 0 \cdot 000025T^2 - 5 \cdot 72T.)$$

5. The heat content change in the reaction, $3/2\mathrm{O}_2=\mathrm{O}_3$ may be represented by

$$\Delta H = 34600 - 2.75T + 0.0028T^2 - 0.0000062T^3.$$

Deduce an expression for the variation of the equilibrium constant of thermal equilibrium. $K_p = p_{O_3}/(p_{O_2})^{3/2}$ may be taken as roughly 0.01 at 2300° K.

.
$$(\Delta F^{\circ} = 34600 + 2.75T \log T - 0.0028T^{2} + 0.00000031T^{3} - 22.4T.)$$

CHAPTER III

THE THIRD LAW OF THERMODYNAMICS

In the last chapter we obtained equations giving the free energy change of gaseous reactions in terms of quantities which, with one exception, are derived from purely thermal data. The exception is the integration constant I, to evaluate which it is necessary to know the value of the equilibrium constant for at least one particular temperature. If I could be calculated or derived from thermal data, we should have in these equations the means of calculating the free energy changes from thermal data alone, i.e. from the measurements of the substances concerned. We should then be able to calculate outright the equilibrium constants of any reactions, for which these quantities are known.

The most general relation between the free energy change and the heat content change in a reaction at constant temperature and pressure is that given by

$$\Delta F = \Delta H - T \Delta S$$
. (78)

The calculation of ΔF from ΔH is thus possible if we have an independent knowledge of ΔS , the entropy change in the reaction. The entropy change in a reaction could be determined if we had values of the entropies of

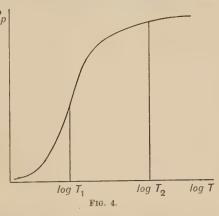
the substances concerned. We have therefore to consider whether it is possible to assign values to the entropies of substances at any given temperature which can be used to determine the entropy changes in reactions.

Entropies Referred to Absolute Zero. In the first place we can evaluate the difference of entropy of a substance between the absolute zero and any given temperature T, if no change of state occurs between these temperatures, by integrating (21), viz. $dS = C_p/T$. dT, between 0 and T. Thus if we denote this entropy difference by S_0^T , we have:

$$S_0{}^T = \!\int_0^T \!\frac{C_{\scriptscriptstyle \mathcal{P}}}{T} \, dT = \!\int_0^T C_{\scriptscriptstyle \mathcal{P}} d\log \, T.$$

The heat capacity of a solid at low temperatures is not a simple function of the temperature, and when the heat

capacities down to very low temperatures are known the integration is best performed graphically. If C_p is plotted against log T the entropy change between any two temperatures T_1 and T_2 (Fig. 4) is equal to the



area enclosed by the curve between the ordinates representing $\log T_1$ and $\log T_2$. To find S_0^T we have to determine the area enclosed by the curve between the ordinate

for $\log T$ and that for T=0 ($\log T=-\infty$). This is usually possible because the heat capacities of solids approach the value zero asymptotically in the vicinity of absolute zero. If the heat capacity is known down to about 40° K. usually the extrapolation to absolute zero can be made without any great error.

When, in passing from absolute zero to the given temperature the substance changes its state by passing from one allotropic modification to another, the entropy change in the change of state (q/T) must be added to the

sum of the $\int C_p \cdot d \log T$ terms. The entropy of a liquid

at any given temperature may similarly be evaluated by determining the entropy change of the solid form of the substance from absolute zero to the melting point, and adding the entropy change on fusion and the entropy change of the liquid between the melting point and the given temperature. The entropy of a gas can be found by including in the same process the entropy change in vaporisation.

The Third Law of Thermodynamics. Consider the reaction

$$A + B = C + D$$

between the four substances A, B, C, D. If these substances have the entropies $(S_0)_A$, $(S_0)_B$, $(S_0)_C$, $(S_0)_D$ at absolute zero, their entropies at a temperature T are

$$(S_0)_A + (S_0^T)_A, \quad (S_0)_B + (S_0^T)_B, \quad (S_0)_C + (S_0^T)_C, (S_0)_D + (S_0^T)_D.$$

The entropy change in the reaction at absolute zero is

$$\Delta S_0 = (S_0)_C + (S_0)_D - (S_0)_A - (S_0)_B,$$

and the entropy change at the temperature T is

$$\Delta S_T = \Delta S_0 + \Sigma S_0^T, \quad \dots (79)$$

where ΣS_0^T is the difference between the sum of the values of S_0^T for the products C and D, and that for the reactants A and B. The values of S_0^T can be determined by heat capacity measurements, as described in the last section. In order to find ΔS_T we therefore need to know ΔS_0 , the entropy change in the reaction at absolute zero.

The Third Law of Thermodynamics states that the entropy change of a reaction between crystalline solids is zero at the absolute zero of temperature.* The justification of this law will be discussed later. If it is true, ΔS_0 is zero for a reaction between crystalline solids, and therefore

$$\Delta S_T = \sum S_0^T$$
,(80)

for such reactions. The entropy change in the reaction can now be determined by evaluating S_0^T for the substances concerned by heat capacity measurements.

This law can be expressed in another way. If the entropy changes of all reactions between crystalline solids are zero at absolute zero, the entropy of a crystalline compound must be the same as that of its crystalline elements at this temperature, so that if we take the entropies of the elements in the crystalline form to be zero, the entropies of crystalline compounds must also be zero at the absolute zero of temperature. We can therefore state the Third Law in the form:

If the entropy of each element in some crystalline form be taken as zero at the absolute zero, the entropy of any pure crystal at the absolute zero is zero.

The values of S_0^T , determined as described in the last section, starting with a crystalline form of the substance

^{*} Lewis and Gibson, J. Amer. Chem. Soc., 39, 2554, 1917; Lewis, Gibson and Latimer, ibid. 44, 1008, 1922.

at absolute zero, can thus be taken as the real values of the entropy at the given temperature T. The following table gives the entropies of a number of substances, as determined in this way, at 25° C.

TABLE III.

Entropies at 25° C. (in calories/degrees).

Elements.

Hydrogen $(1/2H_2, g)$	14.72	Chlorine $(1/2Cl_2, g)$	26:3
Carbon (C, graphite)	1.3	Iron (Fe, s)	6.71
Nitrogen $(1/2N_2, g)$	22.8	Cobalt (Co, s)	$7 \cdot 2$
Oxygen $(1/2O_2, g)$	24.0	Nickel (Ni, s)	$7 \cdot 2$
Sodium (Na, s)	$12 \cdot 2$	Zinc(Zn, s)	9.83
Sulphur (S, rhombic)	$7 \cdot 6$	Bromine (Br_2, l)	16.3
Sulphur (S, monoclinic)	7.8	Silver (Ag, s)	10.25
Cadmium (Cd, s)	11.80	Mercury (Hg, l)	17.8
Indine (I_2, s)	13.19	Lead (Pb, s)	15.53
Iodine (I_2, g)	$31 \cdot 1$		

Compounds.

$H_2O(l)$	-	- 15.9	$NH_3(g)$ -	-	46.7
$\mathrm{HCl}(g)$	-	- 41.2	NaCl(s) -	-	17.2
$\mathrm{HBr}(g)$	-	- 44.9	$\mathrm{KCl}(\hat{s})$ -	-	19.9
$\mathrm{HI}(g)$	-	- 47.8	CuO(s) -	-	9.76
$\mathrm{CH}_4(g)$	**	- 43.4	$\operatorname{HgCl}(s)$ -		$22 \cdot 8$
CO(g)	-	- 45.9	AgCl(s) -	-	23.1
$CO_2(g)$	-	- 51·1	1 0 17		

Origin and Development of the Third Law of Thermodynamics. The free energy change and heat content change in a chemical reaction are related, as we have seen, by the equivalent relations:

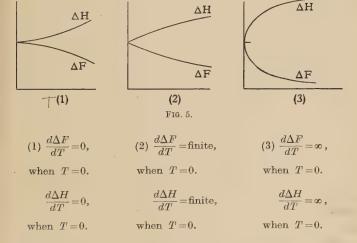
$$\Delta F = \Delta H + T \left(\frac{d\Delta F}{dT} \right)_{p},$$

$$\Delta F = \Delta H - T\Delta S.$$

It was long suspected that some general relation between ΔF and ΔH might be found which would enable

free energy changes to be determined from thermal data. T. W. Richards* in 1902 studied the free energy and heat content changes in a number of galvanic cells and found that they rapidly approached each other as the temperature was lowered. van't Hoff† further studied the matter in 1904, and in 1906 Nernst‡ formulated the relations known as the "Nernst heat theorem."

According to these equations it is evident that unless $d\Delta F/dT$ (or ΔS) is infinite, $\Delta F=\Delta H$ when T=0. Nernst postulated that not only are ΔF and ΔH equal at absolute zero, but they approach equality at this temperature asymptotically. Some of the possibilities are shown in Fig. 5.



^{*} Z. physikal Chem., 42, 129, 1902.

[†] Boltzmann Festschrift, p. 233, 1904.

[‡] Nachr. Kgl. Ges. Wiss., Göttingen; 1, 1906.

Nernst postulated that the actual behaviour of condensed systems (solids or liquids) was that of case (1), i.e.

(1)
$$\frac{d\Delta H}{dT} = 0$$
, in the limit when $T = 0$,(81)

(2)
$$\Delta S = \frac{d\Delta F}{dT} = 0$$
, in the limit when $T = 0$(82)

Since $\frac{d\Delta H}{dT} = \Delta C_p$, (81) implies that the heat capacity change for all reactions in condensed systems is zero when T=0. If this is the case the heat capacity of compounds must be equal to that of the elements from which they are formed. Nernst thought that the heat capacities of all liquids and solids approached the value $C_p=1.5$ calories per gram atom in the vicinity of absolute zero. In 1907 Einstein predicted that the heat capacities would approach, not a finite value, but zero at the absolute zero, and this prediction has since been verified for numerous substances.

The second relation (82) means that the entropy change for all reactions of condensed systems is zero at absolute zero. Nernst supposed that his theorem applied to all reactions of condensed systems, but Planck pointed out that it could not apply to reactions involving solutions. Just as there is an increase of entropy in the mixture of two gases, there is also an entropy increase in the formation of a solution from its components, and there is no reason to suppose that this does not persist to the absolute zero. Lewis and Gibson, in 1920, pointed out that in all probability the entropy of a supercooled liquid is greater than that of a crystalline solid at absolute zero. There is no sharp dividing line between pure liquids and solutions, since liquids may contain more than one

molecular species. A test of this point can be made by measuring the heat capacities of the solid and (supercooled) liquid forms of the substance from the melting point to the vicinity of absolute zero. If ΔS_T is the entropy change of fusion at the temperature T, and ΔS_0 the entropy difference between the solid and supercooled liquid at absolute zero, we have

$$\Delta S_T = \Delta S_0 + \sum S_0^T$$
.

Gibson and Giauque* determined the heat capacities of glycerine as a solid and as a supercooled liquid and found that their results required that ΔS_0 should be an appreciable positive quantity. Simon and Lange† have also shown that amorphous silica has an appreciably greater entropy at absolute zero than the crystalline variety. It is therefore necessary to limit the scope of the law to crystalline substances.

Tests of the Third Law of Thermodynamics. The third law can be tested by comparing the entropy change in a reaction (measured independently) with the difference of the entropies of the products and reactants as calculated on the assumption that the entropies of crystalline solids are zero at absolute zero. The entropy change of a reaction at a temperature T can be determined if the changes of free energy and heat content are known by the equation

$$\Delta S = -\frac{\Delta F - \Delta H}{T}. \quad \dots (83)$$

1. The Conversion of White to Grey Tin. The entropy change for the reaction at 25° C., calculated by (83), is $\Delta S_{298} = -1.87$ units. From the heat capacities the entropy

^{*} J. Amer. Chem. Soc., 45, 93, 1923. † Z. Physik, 38, 227, 1926.

of white tin is $S_{298} = 11 \cdot 17$ and that of grey tin $S_{298} = 9 \cdot 23$, i.e. $\Delta S = -1 \cdot 94$.

2. The reaction Ag + HgCl(s) = AgCl(s) + Hg.

Accurate measurements of the free energy and entropy change of this reaction can be made by measurements of the cell

 $Ag \mid AgCl(s)$, KCl, $HgCl(s) \mid Hg$.

From the electromotive force measurements of Gerke,

 $E_{298} = 0.0455, \ dE/dt = 0.00038.$

The entropy change in the reaction as calculated from these measurements is $\Delta S = +7.8$ cals./degs. The entropy change as determined from the specific heats of the substances, making use of the Third Law, is also +7.8 units (see Table III).

Uses of the Third Law of Thermodynamics. The direct determination of the free energy change of a reaction requires a knowledge of the state of equilibrium. There are many reactions, particularly those involving the formation of organic compounds, for which a state of equilibrium cannot be realised. A knowledge of the free energies of formation of organic compounds would be an extremely valuable aid in estimating the possibilities of effecting reactions. They can be determined indirectly by (78) if the heat contents and entropies of the substance concerned are known. The free energies of a number of compounds have been determined in this way by Parks, Kelley, Anderson, Huffman* and others. Some of their values are given in Table IV. The second column gives the entropy of the compound at 25° C. and the third the entropy of formation from the elements at the same temperature. Knowing ΔH , ΔF for the formation of the

^{*} J. Amer. Chem. Soc., 47, 338, 2094, 1925; 48, 1506, 2788, 1926.

compound from its elements can now be determined. By means of such a table we can find the free energy changes of numerous reactions.

Example. From the free energies of glucose and liquid water we can find the free energy change in the reaction:

$$C_6H_{12}O_6(glucose) = 6C(gr.) + 6H_2O(l)$$

 $\Delta F = -219000 = 0 - 339360.$

The ΔF for the reaction is thus

$$-339360 - (-219000) = -120360.$$

There is thus a large free energy decrease in this reaction, which should be easily effected. Sugars are easily decomposed by strong dehydrating agents such as sulphuric acid.

TABLE IV.

Entropy and Free Energy of Formation of Some Organic Compounds at 25°.

(Parks, Kelley and Huffman, *J. Amer. Chem. Soc.*, **51**, 1972, 1929.)

	S.	ΔS .	$-\Delta H$.	$-\Delta F$.
Methyl alcohol	31.0	54.0	60300	44200
Ethyl alcohol -	38.4	77.5	66300	43200
n-Propyl alcohol	46.1	100.7	73300	43300
iso-Propyl alcohol	43.1	103.7	79000	48100
n-Butyl alcohol -	54.5	123.2	80000	43200
ert-Butyl alcohol -	43.3	132.4	89600	50100
Glycerol	49.7	146.1	159300	115700
Erythritol -	39.8	211.4	215000	152000
Mannitol -	57.0	305.0	317000	226100
Dulcitol	56.0	306.0	318000	226800
Formic acid -	30.7	49.2	99900	85200
Acetic acid -	38.2	72.6	117000	95400
n-Butyric acid -	54.1	118.5	130400	95100
Oxalic acid -	28.7	101.3	196800	166500
Ethyl ether -	60.4	117.3	67300	32300
Acetone	47.8	69.4	57300	36600
Glucose	50.5	281.9	303000	219000

B.C.T. II.

*Entropy of Gases. When the temperature of a gas is increased by a small amount dT at constant pressure, the heat absorbed is $dq = C_p dT$, and the entropy change is

$$dS = \frac{dq}{T} = C_p \frac{dT}{T}.$$

Integrating this we obtain, for a constant pressure,

$$S = S_0 - \int \frac{C_p}{T} \cdot dT$$
,(84)

where S_0 is an integration constant.

When C_{v} is independent of the temperature, we have

$$S = S_0 + C_p \log T$$
,

and combining this with the variation with the pressure which is given for a perfect gas by (57), we have

$$S = S_0 + C_p \log T - R \log p$$
.

The entropy of a monatomic gas for which $C_p = 5/2R$ is thus given by

$$S = S_0 + 5/2R \log T - R \log p$$
.

The entropy constant S_0 is evidently the entropy of the gas at 1° K. and unit pressure.

The value of S_0 for monatomic gases has been calculated by means of statistical mechanics by Sackur* and Tetrode.† The basis of this calculation cannot be given here, but the result is

$$S_0 = R \, \log_e \frac{(2\pi)^{3/2} \, (ke)^{5/2}}{N_0^{3/2} h^3} + 3/2 \, R \, \log \, M,$$

where $k=R/N_0$ is the gas constant per molecule, N_0 the Avogadro number, h the Planck constant, e the base of

^{*} Ann. Physik, (4) 40, 67, 1913.

[†] Ibid. (4), 38, 434, 1912; 39, 255, 1913; also Stern, $Physik.\ Z.$, 14, 629, 1913.

natural logarithms and M the atomic weight of the gas. When the pressure is expressed in atmospheres the result is $S_0 = -2 \cdot 31 + 3/2R \log_e M$ and the entropy of a monatomic gas at 1 atmos. pressure is

$$S = -2.31 + 3/2R \log M + 5/2R \log T$$
.(85)

The following table shows the observed entropies of four monatomic gases at 298 K. and 1 atmos., compared with the values calculated by this equation.

ENTROPY OF MONATOMIC GASES AT 298 K. AND 1 Atmos.

				S ₂₉₈ (Obs.).	S ₂₉₈ (Calc.).
Helium	-	-	-	29.2	30.1
Argon	-	-	-	36.8	37.0
Mercury v	apou	r -	-	41.4	41.8
Cadmium	vapo	ur		39.9	$40 \cdot 1$

The heat capacity of a molecule which consists of more than one atom may be represented by

$$C_p = 5/2R + C_{\text{rot.}} + C_{\text{vib.}}$$
, within

where $C_{\rm rot.}$, $C_{\rm vib.}$, represent the contributions of the rotational and vibrational energy of the molecule. It has been shown that the value of $C_{\rm rot.}$ for diatomic gases is R. Neglecting $C_{\rm vib.}$, which need only be taken into account at high temperatures, the following expression is obtained for the entropy of a diatomic gas

$$S = S_0 + 7/2R \log T - R \log p,$$
 where
$$S_0 = R \log \frac{(2\pi)^{3/2} (ke)^{7/2} \cdot 8\pi^2 J}{N_0^{3/2} k^5 \sigma_0},$$

where J is the moment of inertia of the molecule and σ_0 a symmetry number.*

* For further information see *Treatise on Physical Chemistry*, ed. by Taylor, vol. ii. p. 1450 (1931).

*Chemical Constants. If ΔH is the heat content change in the vaporisation of a gram molecule of a solid at a temperature T, we have

$$\Delta H = \Delta H_0 + \int_0^T \Delta C_p \cdot dT,$$

where ΔH_0 is the heat content change at absolute zero and ΔC_p , the difference of heat capacity between the vapour and the solid.

Introducing this value into (77), we have

$$\frac{d\log p}{dT} = \frac{\Delta H_0}{RT^2} + \frac{1}{RT^2} \int_0^T \Delta C_p \cdot dT.$$

Integrating, we have

log
$$p = -\frac{\Delta H_0}{RT} + \int \frac{\int_0^T \Delta C_p \, dT}{RT^2} + i, \dots (86)$$

where i is the integration constant. The second term can be integrated in parts by making use of the formula $\int A \, dB = A \, B - \int B \, dA \; ; \quad \text{putting} \quad A = \int_0^T \Delta C_p \, . \, dT \; , \quad \text{and} \quad B = -1/RT \; , \text{ we have}$

$$\log p = -\frac{\Delta H_0}{RT} - \frac{\int_0^T \Delta C_p \cdot dT}{RT} + \int \frac{\Delta C_p \cdot dT}{RT} + i,$$
 or, $RT \log p = -\Delta H + T \int \frac{\Delta C_p \cdot dt}{T} + iRT$.

Writing $RT \log p = -\Delta F^{\circ}$, we thus have

$$\Delta F^{\circ} = \Delta H - T \int \frac{\Delta C_p \cdot dT}{T} - iRT, \dots (87)$$

where ΔF° is the difference between the free energy of the gas at unit pressure and that at the solid, both at the temperature T. We can compare this equation with

$$\Delta F^{\circ} = \Delta H - T \Delta S$$
.

where ΔS is the corresponding entropy difference. Evidently

$$\Delta S = \int \frac{\Delta C_p \cdot dT}{T} + iR.$$

Now
$$\Delta S = S_{\text{gas}} - S_{\text{solid}}$$
 and $\Delta C_p = C_{p \text{ gas}} - C_{p \text{ solid}}$,

so that
$$S_{\mathrm{gas}} - S_{\mathrm{solid}} = \int \frac{C_{p \, \mathrm{gas}}}{T} \cdot dT - \int \frac{C_{p \, \mathrm{solid}}}{T} \cdot dT + iR$$
.

By the Third Law,
$$S_{\text{solid}} = \int_0^T \frac{C_{p \text{ solid}}}{T} \cdot dT$$
, so that

$$S_{\text{gas}} = \int \frac{C_{p \text{ gas}}}{T} dT + iR. \qquad \dots (88)$$

Comparing this with (84), we see that

$$iR = S_0,$$
(89)

where S_0 is the entropy constant of the gas (entropy at 1° K. and unit pressure).

i is known as the *chemical constant* of the gas. It can be evaluated by (86) when the heat capacities are sufficiently well known. For monatomic gases it can also be calculated by using the value of S_0 given by (85),

$$\left(i = \frac{S_0}{R} = -\frac{2 \cdot 31}{R} + \frac{3}{2} \log_e M\right).$$

The following table gives a comparison of the values observed and calculated in this way.

CHEMICAL CONSTANTS OF MONATOMIC GASES.

			i (Calc.).	<i>i</i> (Obs.).
Hg	-	-	- 4.37	$4 \hspace{-0.1em}\cdot\hspace{-0.1em} 32 \pm 0 \hspace{-0.1em}\cdot\hspace{-0.1em} 03$
Cd		-	- 3.99	4.15 ± 0.3
Zn	**	-	- 3.64	$3 \cdot 75 \pm 0 \cdot 26$
Pb			- 4.39	$4 \cdot 3 \pm 0 \cdot 2$
A	-	-	- 3.32	3.25 ± 0.02
Na	10	-	- 2.96	$3{\cdot}12\pm0{\cdot}2$
K	-	-	- 3.30	$3{\cdot}42\pm0{\cdot}2$

The chemical constants of a number of diatomic gases as determined by experiment are given below.

CHEMICAL CONSTANTS OF DIATOMIC GASES.

		i (Obs.).	1 .		i (Obs.).
H_2	_	-0.18	HCl	-	3.04
N_2^2	-	3.39	HBr		3.71
O_2	-	4.04	HI	-	4.13
NO	-	4.02	I_2	-	6.62
CO	-	3.45	_		

In Chapter II we integrated the reaction isochore, making use of empirical equations which represent the change of heat capacity with temperature over a wide range of temperature. This range does not extend to low temperatures in the neighbourhood of absolute zero, and the equations obtained for K_p or ΔF° cease to hold at these low temperatures. The integration constants J or I obtained are thus empirical. If the integration were extended to absolute zero, using the actual values of the heat capacities at low temperatures, we should obtain different values of the integration constant.

Making no assumption as to the way in which the heat capacities vary with the temperature, we can integrate the reaction isochore for a gas reaction in the same way as the vapour pressure equation is integrated in (86). Writing

$$\Delta H = \Delta H_0 + \int_0^T \Delta C_{\it p}$$
 , dT ,

where ΔC_p is the heat capacity change in the reaction, and inserting this value of ΔH in (72), we have

$$\frac{d \log K_{p}}{dT} = \frac{\Delta H}{RT^{2}} = \frac{\Delta H_{0}}{RT^{2}} + \frac{1}{RT^{2}} \int \Delta C_{p} \cdot dT.$$

Integrating this, we have

$$\log K_{p} = -\frac{\Delta H_{0}}{RT} + \int \left(\frac{\int_{0}^{T} \Delta C_{p} \cdot dT}{RT^{2}} \right) dT + J, \dots (90)$$

where J is regarded as the true integration constant. Integrating by parts as before, this becomes

$$\log K_{p} = -\frac{\Delta H_{0} + \int_{0}^{T} \Delta C_{p} \, dT}{RT} + \int_{T} \frac{\Delta C_{p}}{RT} \cdot dT + J,$$

or,
$$\Delta F^{\circ} = -RT \log K_p = \Delta H - T \int \frac{\Delta C_p}{T} \cdot dT - JRT$$
.

Comparing this with

$$\Delta F^{\circ} = \Delta H - T \Delta S$$
.

we see that

$$\Delta S = \int \frac{\Delta C_{p}}{T} \cdot dT + JR.$$

Now by (88), we have for each gas concerned

$$S_{
m gas} = \int \!\!\!\! \int \!\!\!\! rac{C_{p}}{T} \, dT + i R, \ J = \Delta i.$$

so that

where Δi is the difference between the sum of the chemical constants of the gases formed and of the reactants.

Alternatively, since $iR = S_0$, we have

$$J = \Delta S_0 / R_1$$
(92)

i.e. the true integration constants of a gaseous reaction is equal to the difference between the corresponding entropy constants of the gases, divided by R. Many of the values of i or J which are to be found in the earlier papers are incorrect, having been derived from too limited a range of temperature.

Examples.

1. The entropies of $N_2(g)$, $H_2(g)$, $NH_3(g)$ at 25 C., as determined by thermal measurements, are 45·6, 29·4, and 46·7 entropy units respectively. The heat content change in the reaction $1/2N_2 + 3/2H_2 = NH_3$ is $\Delta H_{298} = -10985$ cals. Find the free energy change at this temperature. Compare the value obtained with that given in Ex. 3 (p. 36);

$$(\Delta F = -4960 \text{ cals.})$$
, from Ex. $3 = -3910 \text{ cals.})$

2. The heat content change in the reaction

$$Zn + 1/2O_2 = ZnO$$

$$(\Delta F(\mathrm{ZnO}) = -79600 ; \Delta F(\mathrm{reaction}) = +43700)$$

is $\Delta H_{298} = -83000$ cals. The entropy of ZnO at 25° C., as determined by heat capacity measurements, is $10\cdot 4$. Using the data in Table III, find the free energy of formation of zinc oxide. The heat of formation of carbon monoxide being given by $C(gr.) + 1/2O_2 = CO$, $\Delta H_{298} = -26150$ cals., find also the free energy change in the reaction,

ZnO +C(
$$gr$$
.) =Zn +CO. (ΔF (ZnO) = -79600 ; ΔF (reaction) = $+43700$.)

3. The entropy of benzene (C $_6H_6(l))$ at 25° C. is 44.5 cals./degrees. The heat of formation is

$$6C(gr.) + 3H_2 = C_6H_6(l), \Delta H = 11700.$$

Find the free energy of formation of benzene from the elements at this temperature. ($\Delta F = 13950$.)

4. From electromotive force measurements it has been proved that for the reaction

$$1/2\text{Pb} + \text{AgCl}(s) = 1/2\text{PbCl}_2(s) + \text{Ag},$$

 $\Delta F_{298} = -11306$, $\Delta H_{298} = -12585$ cals. Find the entropy change in the reaction, and using the values in Table III, find the entropy of PbCl₂. The entropy of PbCl₂, from heat capacity measurements, is $S_{298} = 33 \cdot 2$.

$$(\Delta S = -4.29 ; S(PbCl_2) = 32.6.)$$

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CHAPTER IV

THE PROPERTIES OF SOLUTIONS

The Components. A solution may be defined as a homogeneous phase of variable composition. It is distinguished from a mixture by its homogeneity, and from a compound by the variability of its composition. That is, we cannot distinguish in it parts which are different from other parts, and we can add small quantities, at least, of any of the substances contained in it without destroying its homogeneity (in some cases we may thereby obtain a supersaturated solution which is unstable). The composition of a solution is stated in terms of its components, which must be chosen in such a way that (1) the amount of each component in the solution may be independently varied, (2) every possible variation in the composition of the solution may be expressed in terms of them. It is often possible to choose alternative sets of components. For example, either SO₃ and H₂O or H₂SO₄ and H₂O might properly be chosen as the components of a solution of sulphuric acid in water. The amount of any one of these pairs of substances in the solution can be varied without affecting the amount of the other, and both pairs are adequate to express every possible variation in the composition of the solution. But although the solution contains sulphur, oxygen and hydrogen, none of these substances can be regarded as components, for their amounts are not *independently* variable. We cannot increase the quantity of sulphur in the solution without also increasing the quantity of oxygen (at least so long as the solution remains a solution of sulphuric acid in water), and we cannot increase the amount of hydrogen without also increasing the amount of oxygen.

It sometimes happens that the physico-chemical properties of solutions obey simpler relations when a particular set of components is chosen. This might be taken as evidence that these components are actually present in the solution as chemical individuals. For example, if it were found that the properties of hydrochloric acid solutions took a particularly simple form (for example, obeyed Raoult's law) when the components are taken as HCl. H₂O and H₂O, this might be regarded as evidence that these are the actual molecular individuals present. But any set of substances which satisfy the conditions stated above may properly be chosen as components, and the choice of any particular set does not imply that these substances are believed to be present as molecules in the solution. For example, if we use SO₂ and H₂O as the components of a sulphuric acid solution, we do not postulate that SO₃ is present in the solution as such. The compounds are merely substances in terms of which all the possible variations of composition can be expressed.

Having chosen the components, the composition of the solution can be expressed in a number of ways. Consider a solution containing w_1 grams of a component A, and w_2 grams of a component B. The following are some of the more common ways of expressing the composition:

(1) Weight fraction. The weight fraction of A is $w_1/(w_1+w_2)$.

- (2) Molar fraction. If M_1 is the molecular weight, according to its chemical formula, of A, and M_2 that of B, the number of mols of A is $w_1/M_1 = n_1$ and that of B, $w_2/M_2 = n_2$, and the molar fraction of A is $\frac{n_1}{n_1 + n_2}$. The molar fraction evidently depends on the molecular formula used.
- (3) Weight concentration. For dilute solutions it is convenient to use as the concentration the amount of one component dissolved in a given weight of the second component. For example, if the solution contains w_2 grams of B in 1000 grams of A, we may use as the weight concentration $m_2 = w_2/M_2$ (sometimes called molar concentration).
- (4) Volume concentration. Weight of substance expressed in mols in (say) 1 litre of the solution.

Partial quantities. Two kinds of quantities are employed in describing the state of a solution (or any other body).

- (1) Intensity factors. Quantities like temperature, refractive index, density, viscosity are independent of the amount of the substance under consideration. They are the same whether we have a gram or a kilogram of the substance in question.
- (2) Capacity factors. Quantities like volume, heat capacity, energy, free energy, which depend on the amount of the substance in question. If the quantity of matter is doubled, the value of each of these quantities is also doubled.

It should be observed that while volume is a capacity factor, the volume per gram (or density) is an intensity factor. The heat capacity is a capacity factor, but the heat capacity per gram (or specific heat) is an intensity factor.

The capacity factors of a solution can usually be directly measured. For example, we can determine the volume, heat capacity, etc., of a given mass of solution. For thermodynamical calculations it is necessary to know also how these quantities vary when the composition is varied. For example, when dealing with a sulphuric acid solution it is necessary to know not only the volume of a given mass, but also the change in volume produced by adding a little sulphuric acid or a little water.

Suppose that we have a solution containing w_1 grams of the component A and w_2 grams of the component B. Let us add a small quantity dw_1 grams of A, which is not sufficient to alter appreciably the relative amounts of A and B. Let the increase in the volume of the solution be dV. Then the increase of volume per unit mass of A added is

$$\frac{dV}{dw_1} = \vec{v}_1;$$

 \bar{v}_1 is called the partial specific volume of A in the solution.

We can equally well make use of molar quantities. Consider a solution containing n_1 mols of A and n_2 mols of B. Suppose that when we add dn_1 mols of A the increase of volume is dV, then

$$\frac{d\,V}{d\,n_1}=\overline{V}_1$$

is the partial molar volume of A in the solution. Similarly, if we add dn_2 mols of B,

$$\frac{d\,V}{dn_2} = \bar{V}_2$$

is the partial molar volume of B. \bar{V}_1 and \bar{V}_2 are evidently intensity factors; they do not depend on the amount of

the given solution, although of course they may vary with its composition.

If we start with a solution containing n_1 mols of A and n_2 mols of B, and add dn_1 mols of A and dn_2 mols of B, the increase of volume is

$$dV = \overline{V}_1 dn_1 + \overline{V}_2 dn_2.$$

Now if dn_1 and dn_2 are in the same proportion as n_1 and n_2 , we may continue making additions of these quantities until we have added finite amounts of A and B, without altering the proportions of A and B in the solution, and therefore without altering \bar{V}_1 and \bar{V}_2 . We can continue adding A and B in these proportions until we have added n_1 of A and n_2 of B, etc., until we have doubled the amount of the original solution. The increase in volume is then

$$V = \overline{V}_1 n_1 + \overline{V}_2 n_2,$$

so that if V is the original volume of the solution, we have

$$V = \bar{V}_1 n_1 + \bar{V}_2 n_2.$$

Generalised Treatment of Solutions. Consider a solution containing n_1 mols of A, n_2 mols of B, n_3 mols of C, etc. Let G be the value of any property which is a "capacity factor." The change in G caused by adding dn_1 of A, dn_2 of B, dn_3 of C, etc., is given by

$$dG = \frac{\partial G}{\partial n_1} \cdot dn_1 + \frac{\partial G}{\partial n_2} \cdot dn_2 + \frac{\partial G}{\partial n_3} \cdot dn_3, \dots (93)$$

where $\frac{\partial G}{\partial n_1} = \overline{G}_1$ represents the increase in G caused by the addition of ∂n_1 of A, when the amounts of B, C, etc., remain constant. Similarly, we may write

$$\frac{\partial G}{\partial n_2} = \overline{G}_2, \quad \frac{\partial G}{\partial n_3} = \overline{G}_3, \text{ etc.},$$

and (93) becomes

$$dG = \bar{G}_1 dn_1 + \bar{G}_2 dn_2 + \bar{G}_3 dn_3 + \dots$$
 (94)

 \overline{G}_1 , \overline{G}_2 , \overline{G}_3 , etc., are the partial molar values of G for the components A, B and C in the solution.

This equation contains quantities of the two kinds. \bar{G}_1 , \bar{G}_2 , etc., are intensity factors, while n_1 , n_2 , etc., are capacity factors. If we double the amount of the solution, \bar{G}_1 , \bar{G}_2 , etc., are unaffected, while n_1 and n_2 are doubled. There is a mathematical theorem (Euler's theorem) which states that a change in the value of a quantity like G, in any small variation of the system, may be completely expressed by summing the products of the intensity factors with the corresponding capacity factors, *i.e.*

Change in G

=(Intensity factor × change of capacity factor).

Equation (94) is thus a complete differential. It represents completely the change in G produced by the infinitesimal additions dn_1 , dn_2 , etc. (Variations involving change of temperature and pressure are not taken into account here.)

Keeping \overline{G}_1 , \overline{G}_2 , \overline{G}_3 , etc., constant by some such process as that described in the last section, we can integrate (94) for a change in which n_1 varies from 0 to n_1 , n_2 from 0 to n_2 , etc., and obtain

$$G = \overline{G}_1 n_1 + \overline{G}_2 n_2 + \overline{G}_3 n_3 + \dots$$
 (95)

Differentiating this generally, without any regard for the significance of the quantities, we have

$$\begin{split} dG = & \overline{G}_1 dn_1 + n_1 d\overline{G}_1 + \overline{G}_2 dn_2 + n_2 d\overline{G}_2 + \overline{G}_3 dn_3 + n_3 d\overline{G}_3 + \text{etc.} \\ \text{But if} \qquad dG = & \overline{G}_1 dn_1 + \overline{G}_2 dn_2 + \overline{G}_3 dn_3, \text{ etc.} \end{split}$$

represents completely an infinitesimal change of G, the sum of the remaining terms must be zero, i.e.

$$n_1 d\bar{G}_1 + n_2 d\bar{G}_2 + n_3 d\bar{G}_3 + \text{etc.} = 0. \dots (96)$$

This is the generalised form of the Duhem-Margules equation.

As an illustration of the meaning of this equation let G be the volume V of a solution having two components. Then (96) becomes

$$n_1 d \bar{V}_1 + n_2 d \bar{V}_2 = 0$$
(97)

for any variation. If the variation considered be a change dN_1 in the molar fraction of A, we have

$$\begin{split} &n_1 \left(\frac{d \, \bar{V}_1}{d \, N_1}\right) + n_2 \left(\frac{d \, \bar{V}_2}{d \, N_1}\right) = 0 \,, \\ &\frac{d \, \bar{V}_1/d \, N_1}{d \, \bar{V}_2/d \, N_1} = -\frac{n_2}{n_1} = -\frac{N_2}{N_1} \,, \, \dots \,. \quad (98) \end{split}$$

or

i.e. when the composition of the solution is varied, the changes in the values of \bar{V}_1 and \bar{V}_2 are inversely proportional to the amounts n_1 and n_2 of the substances present, and of opposite signs, i.e. if $d\bar{V}_1$ is positive, $d\bar{V}_2$ is negative, and vice versa. (See Fig. 8.)

Evaluation of Partial Molar Volumes. To illustrate the methods used for the determination of partial molar quantities we shall give here some methods employed for finding partial molar volumes from the densities of binary solutions.

(1) Direct graphical method for dilute solutions. Consider, for example, an aqueous solution of density d, containing m_2 mols of a solute (molecular weight M_2) in 1000 grams of water. The total weight of this solution is $1000 + m_2 M_2$ grams and its volume,

$$V = (1000 + m_2 M_2)/d.$$

Since the weight of the solvent is constant, the partial molar volume of the solute is $(dV/dm_2)_{1000}$, and this quantity may be determined for any given value of m_2 by plotting V against m_2 and taking the tangent to the

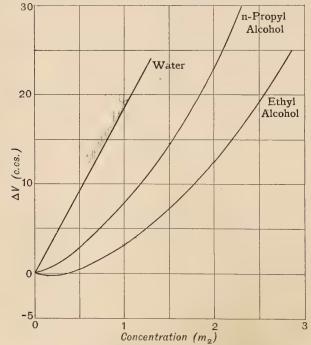


Fig. 6.—Volume changes on addition of lithium chloride (m) to various solvents at 25° .

curve at the point representing the given solution. Instead of V it is more convenient to plot $\Delta V = V - V_0$, where $V_0 = 1000/d_0$ is the volume of the solvent. Fig. 6 shows the values of ΔV for solutions of lithium chloride in several solvents plotted against m_2 .

(2) From the apparent molar volume. Let V be the volume of a solution containing m_2 mols of a solute in 1000 grams of water, and V_0 the volume of 1000 grams of pure water. The "apparent volume" of the solute is $V-V_0$ and its apparent molar volume is $\phi=(V-V_0)/m_2$. This quantity is not itself very useful in thermodynamical calculations, but it can be used in the determination of partial molar volumes.

Writing

$$\phi m_2 = V - V_0$$

and differentiating with respect to m_2 , we have

$$m_2 \cdot \frac{d\phi}{dm_2} + \phi = \frac{dV}{dm_2},$$

$$\frac{d\phi}{d\log m_2} + \phi = \overline{V}_2. \qquad (99)$$

or

The partial molar volume can thus be found by plotting ϕ against $\log m_2$, and taking the slope of the curve at any point. If the value of ϕ at this point be added, we obtain the partial molar volume \bar{V}_2 .

(3) The method of intercepts. Consider a solution of volume V, containing w_1 grams of A and w_2 grams of B. The specific volume (1/d) is $v = V/(w_1 + w_2)$; i.e.

$$V = v(w_1 + w_2).$$

The partial specific volume of A is

$$\vec{v}_1 = \left(\frac{dV}{dw_1}\right)_{w_2} = v + (w_1 + w_2) \left(\frac{dv}{dw_1}\right)_{w_2} \dots$$
 (100)

If we write for the weight fraction of B,

$$W_2 = w_2/(w_1 + w_2),$$

we obtain by differentiation, when w_2 is constant:

$$dW_2 = -\frac{w_2 dw_1}{(w_1 + w_2)^2}$$

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and therefore,

$$(w_1+w_2)\Big(\frac{dv}{dw_1}\Big)_{w_2}=-\,W_2\Big(\frac{dv}{d\,W_2}\Big)\,.$$

Substituting this in (100), we have

$$\bar{v}_1 = v - W_2\left(\frac{dv}{dW_2}\right).$$
(101)

The quantities on the right of this equation can be evaluated by plotting the specific volume v against the

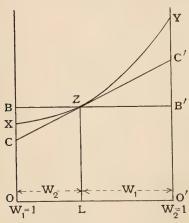


Fig. 7.—Method of Intercepts.

weight fraction W_2 (curve XY, Fig. 7).

Let Z be the point of this curve representing the specific volume of the given solution, the composition of which is represented by the point L. BB' is a horizontal line through Z, so that OB = v. Let CC' be the tangent to the curve at the point Z. The slope of this tangent is equal to

 (dv/dW_2) , so that the distance BC is equal to $W_2(dv/dW_2)$. Thus $OC = v - W_2(dv/dW_2)$, which by (101) is equal to \bar{v}_1 . The partial specific volume of A in the given solution L is therefore equal to the intercept OC made by the tangent at Z on the axis representing pure A ($W_1 = 1$). Similarly it can be shown that the partial specific volume of B in the given solution is equal to the inter-

cept O'C' made by the tangent on the axis representing pure $B(W_2 = 1)$.

The partial molar volumes can of course be found by multiplying the partial specific volumes by the molecular weights of the substances. They could alternatively be determined by plotting the molar volume of the solution against the molar fraction and taking intercepts as above. (If the volume of a solution containing n_1 mols of A and n_2 mols of B is V, the molar volume is $V/n_1 + n_2$.)

Fig. 8 shows the differences between the partial molar volumes of water and alcohol in their solutions and

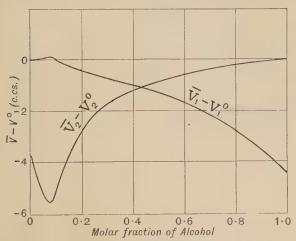


Fig. 8,—Partial molar volumes of water and alcohol in their solutions.

molar volumes V_1° and V_2° of the pure liquids. Notice that when \overline{V}_1 increases, \overline{V}_2 decreases, and vice versa. Also when N_2 is small compared with N_1 , the change of \overline{V}_2 is large compared with that of \overline{V}_1 , and when N_1 is

small compared with N_2 , the change of \overline{V}_1 is large compared with that of \overline{V}_2 , as is required by (98).

(4) Calculation of partial volumes of the second constituent from those of the first. Writing (97) in the form

$$d\, \bar{V}_2 = -\frac{n_1}{n_2} d\, \bar{V}_1,$$

and integrating between the limits V_1 and V_1 , we have

$$\overline{V}_{2}{}^{\prime\prime} - \overline{V}_{2}{}^{\prime} = - \int_{\overline{V}_{1}{}^{\prime\prime}}^{\overline{V}_{1}{}^{\prime\prime}} \frac{n_{1}}{n_{2}} d\, \overline{V}_{1}.$$

i.e. we can determine the change of \overline{V}_2 for a binary solution over a range of concentrations for which values of \overline{V}_1 are known. If we plot the molar ratios (n_1/n_2) of the solutions against the values of \overline{V}_1 , the area enclosed by the curve between the values \overline{V}_1 and \overline{V}_1 is equal to \overline{V}_2 – \overline{V}_2 .

Heats of Solution. Suppose that when we make a homogeneous solution by mixing n_1 mols of a substance A and n_2 mols of a substance B, keeping the temperature constant, a quantity of heat q is absorbed. q is the total heat of formation of the solution or the total heat of solution. If, when we add to the solution so obtained a small amount dn_1 of A, the heat absorbed is dq, then

$$\frac{dq}{dn_1} = \bar{q}_1$$

is the partial or differential heat of solution of A in the given solution. Similarly

$$\frac{dq}{dn_2} = \bar{q}_2$$

is the partial heat of solution of B in the given solution. It is assumed of course that the quantities added are so small in comparison with the amount of the solution that

they do not appreciably affect the concentration. The following table gives the partial molar heats of solution of water (A) and sulphuric acid, $\mathrm{H_2SO_4}\left(B\right)$ in sulphuric acid solutions.

TABLE V.

PARTIAL HEATS OF SOLUTION IN SULPHURIC ACID

SOLUTIONS AT 18° (calories).

$egin{array}{l} ext{Molar} \ ext{Fraction of} \ ext{H}_2 ext{SO}_4. \end{array}$	Partial Heat of Solution of H ₂ O.	Partial Heat of Solution of H ₂ SO ₄ .	$\begin{array}{c} \text{Relative} \\ \text{Partial Heat} \\ \text{Content of} \\ \text{H}_2\text{O}. \end{array}$	Relative Partial Heat Content of H ₂ SO ₄ .
N_2	\overline{q}_1	\overline{q}_{2}	L_1	\overline{L}_2
0.00	0.0	-20200	0	0
0.05	-43.7	-16070	- 43.7	4130
0.10	-293.3	-12470	-293.3	7730
0.20	-1000	- 9010	-1000	11190
0.30	- 1910	-6230	-1910	13970
0.40	- 3060	-4040	- 3060	16160
0.50	-4850	-1890	-4850	18310
0.60	- 6300	- 670	-6300	19530
0.70	-7010	-290	-7010	19910
0.80	-7490	-102	- 7490	20092
0.90	-7870	-47	-7870	20153
1.00	-8220	0	-8220	20200

The total heat of solution can easily be found when the partial heats of solution are known. The heat absorbed when small additions dn_1 and dn_2 are made to the solution is:

$$dq = \bar{q}_1 dn_1 + \bar{q}_2 dn_2, \dots (102)$$

and therefore, we can obtain by integration, as in (95),

$$q = \bar{q}_1 n_1 + \bar{q}_2 n_2.$$
(103)

Example. What is the total heat of formation of a solution containing 0.1 mols of sulphuric acid and 1 mol of water? By (103), using the values given in Table V for $N_2 = 0.10$,

$$q = -293 \cdot 3 - (0.1 \times 12470) = -1540$$
 calories.

Heats of dilution can also be calculated when the partial heats of solution in the initial and final solutions are known. Suppose that we start with a solution of n_1 mols of A and n_2 mols of B and add n_3 mols of A. The total heat of dilution is evidently equal to the difference between the heats of formation of the final and that of the initial solution. Let \bar{q}_1' , \bar{q}_2' , be the partial heats of solution in the original solution. Then its heat of formation is $q' = n_1 \bar{q}_1' + n_2 \bar{q}_2'$

Similarly if $\bar{q}_1^{\ \prime\prime}$, $\bar{q}_2^{\ \prime\prime}$ be the partial the final solution, its heat of formation is $q^{\prime\prime}=(n_1+n_3)\bar{q}_1^{\ \prime\prime}+n_2\bar{q}_2^{\ \prime\prime},$ Similarly if $\bar{q}_{1}^{\ \prime\prime}$, $\bar{q}_{2}^{\ \prime\prime}$ be the partial heats of solution in

$$q'' = (n_1 + n_3)\bar{q}_1'' + n_2\bar{q}_2''$$

and the heat absorbed in the dilution is

$$q^{\prime\prime} - q^\prime = (n_1 + n_3) \bar{q}_1^{\ \prime\prime} + n_2 \bar{q}_2^{\ \prime\prime} - n_1 \bar{q}_1^{\ \prime} - n_2 \bar{q}_2^{\ \prime}.$$

Example. What is the heat absorbed if we start with a solution containing 0.1 mols of sulphuric acid and 1 mol of water and add 1 mol of water?

The heat of formation of the original solution, as we have seen in the previous example, is q' = -1540 calories. The heat of formation of the final solution $(\tilde{N}_2 = 0.05)$ is

$$q'' = -2 \times 43.7 - (0.1 \times 16070) = -1694$$
 calories.

The heat of dilution is thus

$$-1694 - (-1540) = -154$$
 calories,

i.e. 154 calories are evolved.

Heat Contents of Solutions. If H is the heat content of a solution containing n_1 mols of A and n_2 mols of B, and H_1° , H_2° the molar heat contents of A and B at the same temperature and pressure, the heat absorbed in the formation of the solution is

$$q = H - n_1 H^{\circ}_1 - n_2 H^{\circ}_2$$
.(104)

The partial heat content of A in the given solution may be defined as

$$\bar{H}_1 = \left(\frac{dH}{dn_1}\right)_{n_2}, \quad \dots (105)$$

i.e. the increase of H, caused by the addition of a small quantity of A to the solution, per mol of A added. The heat absorbed when dn_1 mols of A are added to the solution (at constant T and P) is equal to the increase in the heat content of the solution less the heat content of the substance added, *i.e.*

$$dq = \tilde{H}_1 dn_1 - H^{\circ}_{1} dn_1.$$

Since $\frac{dq}{dn_1} = \bar{q}_1$ is the partial heat of solution of A in the

given solution,
$$\tilde{q}_1 = \tilde{H}_1 - H^{\circ}_1$$
,(106)

i.e. the partial heat of solution is equal to the difference between the heat content in the solution and the heat content of the pure substance.

The values of the partial heat contents of the components of solutions can conveniently be tabulated by giving the difference between the partial heat content in a given solution and the heat content of the substance in some suitable standard state at the same temperature and pressure. These quantities are called relative partial heat contents. For most purposes the use of one or other of the following standard states is sufficient.

(1) The standard state of a component is taken to be the pure substance in a specified form at the given temperature and pressure. Thus with aqueous solutions it is convenient to take as the standard state of water, pure liquid water at the same temperature and pressure. The relative heat content is then

$$\bar{L}_1 = \tilde{H}_1 - H^{\circ}_{1},$$

where H°_{1} is the heat content of the pure substance, and thus by comparison with (106), it is evident that when this choice is made

 $\bar{L}_1 = \bar{q}_1, \dots (107)$

or, the relative heat content is equal to the partial heat of solution of the pure substance.

(2) The standard state of a substance is taken to be an infinitely dilute solution in the given solvent.

If \bar{H}°_{2} is the partial molar heat content of the substance S, at infinite dilution, the relative heat content according to this definition is

$$\bar{L}_2 = \bar{H}_2 - \bar{H}^{\circ}_2$$
.

If H_2° is the heat content of the same substance in a pure state, we may write,

where \bar{q}_2° is its partial heat of solution in an infinitely dilute solution.

In many cases, particularly in dealing with dilute solutions, it is convenient to use the first standard state for one component (the solvent) and the second for the other. Table V shows the relative heat contents of water and sulphuric acid in their solutions, at 25° C., the standard states being (1) for water, the pure liquid; (2) for sulphuric acid, an infinitely dilute solution in water. The relative heat content of water in any solution is thus equal to its partial heat of solution, and that of $\rm H_2SO_4$, by (108), is obtained by subtracting (-20200) calories from the partial heat of solution of sulphuric acid.

Applying (96) to a binary solution, we have

$$n_1 d\tilde{H}_1 + n_2 d\tilde{H}_2 = 0, \dots (109)$$

and if the relative heat contents as defined above be taken

$$n_1 d\bar{L}_1 + n_2 d\bar{L}_2 = 0....(110)$$

When the partial heat contents of one component are known for a range of concentrations it is thus possible to determine the changes of the partial heat contents of the second component over the same range.

Partial molar heat capacities. If C_p is the heat capacity of a solution containing n_1 mols of a substance A, n_2 mols of B, etc., the partial molar heat capacity of A in the solution is defined as

$$\vec{C}_{p_1} = \left(\frac{dC_p}{dn_1}\right)_{n_2, n_3, \text{ etc.}}$$
.....(111)

The total heat capacity of the solution is

$$C_p = n_1 \overline{C}_{p_1} + n_2 \overline{C}_{p_2} + n_3 \overline{C}_{p_3} + \text{etc.}....(112)$$

and by (96) we have the following relation between the changes of the partial heat capacities of the different components:

$$n_1 d\vec{C}_{p_1} + n_2 d\vec{C}_{p_2} + n_3 d\vec{C}_{p_3} + n_4 d\vec{C}_{p_4} \dots = 0. \dots (113)$$

By (7), the rate at which the heat content of the whole system changes with the temperature is equal to its heat capacity, or $\frac{\partial H}{\partial t} = C_p$. Differentiating this with respect to n_1 (n_2 , n_3 , etc., being constant), we have

$$\frac{\partial^2 H}{\partial t \;.\; \partial n_1} = \frac{\partial C_{p}}{\partial n_1} = C_{p_1}.$$

But

$$rac{\partial H}{\partial n_1} = \overline{H}_1 \quad ext{and} \quad rac{\partial^2 H}{\partial n_1 \cdot \partial t} = rac{\partial \overline{H}_1}{\partial t},$$

therefore, comparing these two expressions, which only differ in the order of differentiation, we have

$$\frac{\partial \bar{H}_1}{\partial t} = \bar{C}_{p_1}. \qquad (114)$$

Since

$$\bar{L}_1 = \bar{H}_1 - H^\circ_{1},$$

we obviously have

$$\frac{d\bar{L}_{1}}{dt} = \frac{d\bar{H}_{1}}{dt} - \frac{dH^{\circ}_{1}}{dt} = \bar{C}_{p_{1}} - C^{\circ}_{p_{1}}, \dots (115)$$

where $C_{p_1}^{\circ}$ is the corresponding heat capacity in the standard state. In order to find the variation of the partial (or relative) heat contents with the temperature, it is thus necessary to know the corresponding partial heat capacities.

Examples.

- 1. In a thallium amalgam in which the molar fraction of thallium is 0.400 the partial molar heats of solution of thallium and mercury are +715 cals, and -232 cals, respectively. Find the total heat of solution. The partial heat of solution of thallium in a very large quantity of mercury is -805 cals. Find the partial molar heat content of thallium in the given amalgam relative to an infinitely dilute amalgam. $(q=147 \text{ cals.};\ L_2=+1520 \text{ cals.})$
- 2. The quantities of heat evolved (per mol) when small quantities of sulphuric acid and water are added to a solution containing 50 mols per cent. of each are 1890 and 4850 cals., and the same quantities for a solution containing 75 mols per cent. water are 7520 and 1450 cals. Find (1) the heat evolved when a mol of water and a mol of sulphuric acid are mixed; (2) the heat evolved when two mols of water are added to the solution. (1) 6740 cals., (2) 5130 cals.)

- 3. The heat absorbed per mol when water is added to a large quantity of a saturated solution of sodium chloride is 11·5 cals., and that absorbed when salt is added to the solution obtained is 517 cals. per mol. Find the heat of solution of a mol of sodium chloride in sufficient water to make a saturated solution, 9·04 mols. (621 cals.)
- *4. Criticize the following suggested method of finding the "volumes of the constituents of a solution." In 100 volumes of a solution of x volumes of one substance A and y volumes of a substance B, where the sum of x and y are not a hundred, there must be some factor a by which the original volume x of A is expanded or contracted and another factor b by which the original volume y of B is contracted or expanded. Therefore we can write

$$ax + by = 100$$
.

Similarly for another solution of A and B, which also occupies 100 volumes,

$$a'x' + b'y' = 100.$$

If x is very near x' and y very near y', no great error is made if we assume that a=a' and b=b'; and thus +a and b may be determined by solving the two equations. What are the quantities a and b?

*5. At 24.90° the density $(d_4^{24.9})$ of methyl alcohol is 0.786624, and the following table gives the densities of some lithium chloride solutions in this solvent at the same temperature. Find the apparent molar volumes of lithium chloride in the solutions (m = mols LiCl in 1000 gms. methyl alcohol).

m.		d.
0.0638		0.788826
0.0834	ni	0.789478
0.1079		0.790309
0.2183		0.793916

(See J. Chem. Soc., p. 933, 1933, for results.)

CHAPTER V

THE FREE ENERGY OF SOLUTIONS

Partial Molar Free Energies. Since the free energy of a solution is also a "capacity factor," the partial free energies of the components may be determined by the methods of Chapter IV. Suppose that a solution contains n_1 mols of S_1 , n_2 mols of S_2 , n_3 mols of S_3 , ... and n_n mols of S_n . The partial molar free energies are defined as

$$\begin{split} \overline{F}_1 = & \left(\frac{dF}{dn_1}\right)_{T,~p,~n_2,~\text{etc.}} \\ \overline{F}_2 = & \left(\frac{dF}{dn_2}\right)_{T,~p,~n_1,~n_3,~\text{etc.}} \text{, and so on.} \end{split}$$

When dn_1 mols of S_1 , dn_2 mols of $S_2 \dots dn_n$ mols of S_n are added to the solution the increase of its free energy can therefore be written

$$dF = \bar{F}_1 dn_1 + \bar{F}_2 dn_2 + \bar{F}_3 dn_3 \dots + \bar{F}_n dn_n \dots (116)$$

Applying (95) and (96), we have then

and

$$F = \overline{F}_1 n_1 + \overline{F}_2 n_2 + \overline{F}_3 n_3 \dots + \overline{F}_n dn_n, \qquad (117)$$

$$n_1 d\overline{F}_1 + n_2 d\overline{F}_2 + n_3 d\overline{F}_3 \dots + n_n d\overline{F}_n = 0. \qquad (118)$$

The partial free energies are fundamentally important in chemical thermodynamics because the conditions of equilibrium of the parts of a heterogeneous system are most conveniently stated in terms of them. It has been shown that the conditions of thermal and mechanical equilibrium of a material system are that the temperature and, provided that the system is not so large that the effect of gravitational forces becomes appreciable, the pressure must be the same throughout. The condition of chemical equilibrium is contained in the statement that the partial free energy of each component must be the same in every phase in which it is actually present. A proof of this proposition is given in the following section.

Conditions of Equilibrium in Heterogeneous Systems. Consider for simplicity the case of a system of two phases, both containing the components $S_1, S_2, S_3 \dots S_n$. The quantities of these components in the first phase are n_1' , n_2' , n_3' , etc., and the quantities in the second phase n_1'' , n_2'' , n_3'' , etc. Then the variation of the free energy of the first phase when the quantities of its components are varied by small amounts $\delta n_1'$, $\delta n_2'$, etc., at constant temperature and pressure, is given by

$$\delta F' = \bar{F}_{1}' \delta n_{1}' + \bar{F}_{2}' \delta n_{2}' + \bar{F}_{3}' \delta n_{3}' \dots \bar{F}_{n}' \delta n_{n}',$$

and similarly we may write for similar variations of the second phase

$$\delta F^{\prime\prime} = \bar{F}_{1}^{\ \prime\prime} \delta n_{1}^{\ \prime\prime} + \bar{F}_{2}^{\ \prime\prime} \delta n_{2}^{\ \prime\prime} + \bar{F}_{3}^{\ \prime\prime} \delta n_{3}^{\ \prime\prime} \dots + \bar{F}_{n}^{\ \prime\prime} \delta n_{n}^{\ \prime\prime},$$

where \bar{F}_1 is the partial free energy of S_1 in the first phase, and \bar{F}_1 its value in the second phase, etc. We shall suppose that the temperature and pressure are the same in both phases, since it has already been shown that this is a necessary condition. This being the case, it is necessary by (41) that the variation of the free energy of the system shall be zero or positive for all possible variations

of the state of the system which do not alter its temperature and pressure, *i.e.*

$$(\delta F' + \delta F'') \ge 0$$

for all such variations.

Let us consider what variations are possible. We will limit ourselves at first to the case in which none of the components can be formed out of other components. The possible variations are then those in which small quantities of the different components pass from one phase to the other. All such variations must be in accordance with the equations:

$$\begin{cases} \delta n_1{}' + \delta n_1{}'' = 0, \\ \delta n_2{}' + \delta n_2{}'' = 0, \\ \dots \\ \delta n_n{}' + \delta n_n{}'' = 0, \end{cases}$$
(119)

i.e. the total amount of each component is a constant. The change of free energy of the whole system in any variation in which the temperature and pressure remain unchanged is given by

$$\begin{split} \delta F = & \delta F' + \delta F'' \\ = & \bar{F}_{1}' \delta n_{1}' + \bar{F}_{2}' \delta n_{2}' + \bar{F}_{3}' \delta n_{3}' \dots + \bar{F}_{n}' \delta n_{n}' \\ + & \bar{F}_{1}'' \delta n_{1}'' + \bar{F}_{2}'' \delta n_{2}'' + \bar{F}_{3}'' \delta n_{3}'' \dots + \bar{F}_{n}'' \delta n_{n}''. (120) \end{split}$$

This quantity must be zero or positive for all possible values of δn_1 , δn_2 , etc. Since, by (119), $\delta n_1 = -\delta n_1$, etc., we may therefore write as the condition of equilibrium

$$\begin{split} (\bar{F}_{1}' - \bar{F}_{1}'') \delta n_{1}' + (\bar{F}_{2}' - \bar{F}_{2}'') \delta n_{2}' \dots \\ + (\bar{F}_{n}' - \bar{F}_{n}'') \delta n_{n}' &\geq 0. \dots (121) \end{split}$$

If, as we have supposed, every component is present in both phases, its amount in either phase may either increase or decrease, i.e. dn_1' , dn_2' , etc., may be separately either positive or negative. (121) can therefore only be generally true if

$$\bar{F}_{1}' = \bar{F}_{1}'', \ \bar{F}_{2}' = \bar{F}_{2}'', \dots \bar{F}_{n}' = \bar{F}_{n}''. \dots \dots (122)$$

It is thus necessary for equilibrium that the partial free energy of each component shall be the same in both phases. It is easy to extend this argument to a system containing any number of distinct phases and to show that it is necessary for equilibrium that the partial free energy of each component shall have the same value in every phase in which it is actually present.*

We have supposed that every component is present in all the phases. It may happen that some of the components are entirely absent from certain phases. There is then no necessary equality like those in (122), but the partial free energy in this phase cannot be *less* than that in other parts of the system in which the component is present.†

Finally there is the case in which some components can be formed out of others. Suppose that the components C, D can be formed out of the components A, B according to the equation

$$aA + bB = cC + dD$$
,(123)

* The partial free energy of a component in a phase which consists of that component only is of course equal to its molar free energy in that state.

 \dagger For if a component is absent from any phase its amount may be increased but cannot be decreased. δn for the given component in this phase may thus have positive but it cannot have negative values.

where a, b, c, d represent the numbers of formula weights of these substances which enter into the reaction. It is easy to prove as above, by considering variations in which the amount of each component remains constant that $\bar{F}_1' = \bar{F}_1''$, $\bar{F}_2' = \bar{F}_2''$, etc. (If (122) is satisfied for every possible variation it must be satisfied for any selection of the possible variations.) Thus (120) can be written

$$\bar{F}_A \Sigma \, \delta n'_A + \bar{F}_B \Sigma \, \delta n'_B + \bar{F}_C \Sigma \, \delta n'_C + \bar{F}_D \Sigma \, \delta n'_D = 0,$$

and where $\Sigma \delta n'_A$ is the total change in the amount of A throughout the system. Evidently the quantities $\Sigma \delta n_{A'}$, $\Sigma \delta n_{B'}$, $\Sigma \delta n_{C'}$, $\Sigma \delta n_{D'}$ must be such that (123) is satisfied, *i.e.* they must be proportional to a, b, -c, -d. We therefore have

$$a\bar{F}_A + b\bar{F}_B = c\bar{F}_C + d\bar{F}_D.$$
(124)

The relation between the partial free energies is thus the same as that between the chemical formulae of the substances concerned (compare the similar deduction for gases, p. 31).

Determination of the Partial Free Energy from the Vapour Pressure. When a liquid and its vapour are in equilibrium, the partial free energy of a volatile component must be the same in both phases, and its value in the liquid may be determined by finding its value in the vapour. Consider a binary solution containing the components S_1 , S_2 whose partial pressures in the vapour are p_1 , p_2 . If the vapour has the properties of a perfect gas mixture, the partial molar free energy of S_1 in the vapour, by (59), is

$$\bar{F}_1 = (F_g)_1 + RT \log p_1,$$

wind present.

and similarly if p_1° is the partial pressure of the pure liquid S_1 at the same temperature, its partial molar free energy is

 $F_{1}^{\circ} = (F_{g}^{\circ})_{1} + RT \log p_{1}^{\circ}.$

Combining these two equations, we have

$$\vec{F}_1 = \vec{F}_1 + RT \log p_1/p_1^{\circ}....(125)$$

Similarly for the second component,

$$\overline{F}_2 = F_2^{\circ} + RT \log p_2/p_2^{\circ}$$
.(126)

It must be observed that in these equations the partial free energy obtained is that of a gram molecule in the vapour phase, and has nothing to do with the molecular weight in the liquid.

If the solution contains n_1 mols of S_1 and n_2 mols of S_2 (taking any convenient molecular weights), we have by (118), for a constant temperature variation:

$$n_1 d\bar{F}_1 + n_2 d\bar{F}_2 = 0$$
,

or introducing the values of (125), (126),

$$n_1 d \log(p_1/p_1^{\circ}) + n_2 d \log(p_2/p_2^{\circ}) = 0,$$

or since p_1° and p_2° are constant, dividing by dn_2 , we obtain,

$$n_1 \left(\frac{d \log p_1}{d n_2}\right)_{n_1} + n_2 \left(\frac{d \log p_2}{d n_2}\right)_{n_1} = 0.$$
 (127)

It is evident from these equations, which are forms of the Duhem-Margules relation, that when a small quantity of S_2 is added to the solution:

- (1) If $\log p_2$ increases, $\log p_1$ decreases.
- (2) The magnitude of the change of $\log p_2$ is inversely proportional to the amount of S_2 in the solution. Thus if n_1 is large compared with n_2 , the change of $\log p_1$ is small, and of the opposite sign to that of $\log p_2$.

B.C.T. II.

Writing (127) in the form

$$d\log p_1 = -\frac{n_2}{n_1}d\log p_2,$$

and integrating from p_2 to p_2' , we have

$$\log p_1' - \log p_1 = -\int_{p_2}^{p_2'} \frac{n_2}{n_1} d \log p_2. \dots (128)$$

Thus if p_2 is known as a function of the molar ratio for a range of solutions the variation of p_1 over the same range can be calculated.

Variation of the Partial Free Energy with Composition in Very Dilute Solutions. This variation cannot be deduced a priori by thermodynamical arguments, but must in general be established by experimental study. Concentrated solutions exhibit a wide variety of behaviour, and no generalisation can be made, but in very dilute solutions the researches of van't Hoff, Raoult and others on the vapour pressures, freezing points, boiling points, osmotic pressures of these solutions established the law that equal numbers of solute molecules in a given quantity of a solvent cause the same change of all these magnitudes. Since no independent determination of the molecular weight in solution is available, this law depends on the fact that it has been shown to hold in a very considerable number of cases when the molecular weight is that required by the chemical formula. The evidence is so strong that in cases of apparent disagreement it may be assumed that the molecular weight employed is incorrect, and the law may be used to establish the molecular weights in solution.

Since all the properties listed above depend on the effect of the solute on the partial free energy of the

solvent, we may state that in very dilute solutions equal numbers of solute molecules in a given quantity of solvent cause the same change in the partial free energy of the solvent. Since the change produced by a given amount of solute is obviously inversely proportional to the amount of solvent, we can therefore write

$$\frac{d\bar{F}_1}{dn_2} = -\frac{A}{n_1}, \dots (129)$$

where n_2 is the number of mols of the solute, n_1 is the amount of the solvent * and A a constant.

Although for convenience we have expressed the amount of the solvent as a molar quantity n_1 , and have used the corresponding molar free energy, \bar{F}_1 , we are involved in no assumption as to the molecular weight of the solvent in the liquid state, for $n_1 d\bar{F}_1$ is independent of the unit of quantity employed. If the molecular weight used were doubled, $d\bar{F}_1$ would be doubled and n_1 halved and the product $n_1 d\bar{F}_1$ would be unchanged.

The experimental behaviour of dilute solutions shows that, provided the molecular weight of the solute is chosen properly, A is independent of the solvent and has the universal value RT. This identification of A with RT is the simplest and most general way of stating van't Hoff's analogy between the laws of dilute solutions and of gases. Writing $d\bar{F}_1/dn_2 = -RT/n_1$, we obtain by integration $\bar{F}_1 = \bar{F}_1^\circ - RTn_2/n_1$(129a)

Since by (118), $n_1 d\bar{F}_1 = -n_2 d\bar{F}_2$, we also have

$$\frac{n_2 \, d\bar{F}_2}{dn_2} = \frac{d\bar{F}_2}{d\log n_2} = RT.$$

^{*} Expressed in terms of the same units as F_1 .

The integral of this equation may be written in the form $\bar{F}_2 = \bar{F}^{\circ}_2 + RT \log (n_2/n_1), \dots (130)$

where \bar{F}° is a constant. If the quantity of the solvent

is 1000 gms., n_2/n_1 may be replaced by m_2 . Also in dilute solutions n_2/n_1 is practically equal to the molar fraction

$$N_2 = n_2/n_1 + n_2.$$

Derivation of Raoult's Law. The change of vapour pressure, freezing point, etc., of the solvent produced by a solute can easily be derived from these equations. We will give the derivation of Raoult's Law as an example. Putting $d\tilde{F}_1 = RT$. $d \log p_1 = RT$. dp_1/p_1 , in (129) and giving A its value RT, we have

$$\frac{dp_1}{p_1} = -\frac{dn_2}{n_1}.$$

When n_2 is very small this may be written in the form

$$\frac{p_1^{\circ} - p_1}{p_1} = \frac{n_2}{n_1}, \dots (131)$$

i.e. the fractional lowering of the vapour pressure of the solvent is equal to the ratio of the number of mols of solute to that of the solvent. In finding this molar ratio it is important to observe that while the molecular weight of the solute is that in the solution (which is fixed by the criterion that equal numbers of solute molecules must cause the same lowering of the free energy of the solvent), the molecular weight of the solvent is that in the vapour phase. This is the case because the equation $d\bar{F}_1 = RT$. $d \log p_1$ refers to the vapour. nothing in this equation which refers to the molecular weight of the solvent in the liquid state.

Distribution of a solute between two solvents. An excellent illustration of the effect of the molecular weight of the solute in solution on its thermodynamic behaviour is afforded by considering its distribution between two phases. Suppose first that the solute has the same molecular weight corresponding to the formula A in the two solvents. In very dilute solution its partial free energy in the two solvents is given by

$$\begin{split} & \bar{F}_A = & \bar{F}^\circ_A + RT \cdot \log m_A, \\ & \bar{F}_{A^{'}} = & \bar{F}^\circ_{A^{'}} + RT \cdot \log m_{A^{'}}, \end{split}$$

where \bar{F}°_{A} , \bar{F}°_{A} are the stardard free energies for the two solvents. Since for equilibrium its partial free energy must be the same in two solvents, we have

$$ar{F}^{\circ}{}_A+RT$$
 . $\log m_A=ar{F}^{\circ}{}_A{}'+RT$. $\log m_A{}',$ $m_A/m_A{}'=e^{(ar{F}^{\circ}}A'-F^{\circ}A)/RT=K,$

or

where K is usually known as the distribution constant.

Now suppose that the solute exists as simple molecules A in the first solvent and as double molecules A_2 in the second. We have then,

$$\begin{split} & \bar{F}_A = \bar{F}^{\circ}{}_A + RT \cdot \log m_A, \\ & \bar{F}_{A_2} = \bar{F}^{\circ}{}_{A_2} + RT \cdot \log m_{A_2}; \end{split}$$

where the quantities in the second equation are all obtained by the use of the molecular weight corresponding to A_2 . Since the amount to which the second equation applies is twice that of the first, the condition of equilibrium is $\bar{F}_{A_2} = 2\bar{F}_A$; and therefore the distribution law is

$$m_A{}^2/m_{A_2} = e^{(\bar{F}^{\circ}A_2 - 2F^{\circ}A)/RT} = K.$$

The Activity. The equations of the preceding sections only apply to extremely dilute solutions, and in more concentrated solutions very considerable deviations often occur. In such solutions it is convenient to express the partial free energies of the components in terms of their activities, which are defined by equations of the type:

$$\bar{F}_2 = \bar{F}_2^{\circ} + RT \log a_2, \dots (132)$$

where \bar{F}_{2}° , the partial free energy of S_{2} in the solution for which the activity has been taken as unity, may be termed the standard free energy under the conditions defined. In different cases it is convenient to adopt different conventions.

(1) Activity of the solute in dilute solutions. The variation of the partial molar free energy of a solute S_2 is given at small concentrations, if the molecular weight is chosen correctly, by $\overline{F}_2 = \overline{F}_2^{\circ} + RT \log m_2$.

In solutions in which this limiting equation is not obeyed we may write

$$\overline{F}_2 = \overline{F}_2 + RT \log \alpha_2, \dots (132a)$$

where $a_2 = m_2$ when m_2 is very small. The ratio $a_2/m_2 = f_2$ is the activity coefficient. If the concentration is expressed as the molar fraction and not in terms of m, we may write for the limiting law:

$$\bar{F}_2 = (\bar{F}_2^{\circ})' + RT \log N_2,$$

and for actual solutions

$$\bar{\boldsymbol{F}}_{2} = (\bar{\boldsymbol{F}}^{\circ}_{2})' + RT \log a_{2},$$

and the activity coefficient is $f_2 = \alpha_2/N_2$. Evidently $f_2 = 1$, when m_2 (or N_2) is very small.

It is important to observe that it is only possible for a_2 to become equal to m_2 (or N_2) when m_2 is small if the molecular weight of the solute which is used in calculating the molecular concentrations is that which satisfies $d\bar{F}_1/dn_2 = -RT/n_1$.

(2) Activity of the solvent. In this case it is usually more convenient to take the activity of the solvent (S_1) as unity in the pure liquid. Then writing

$$\bar{F}_1 = F_1^{\circ} + RT \log a_1, \dots (132b)$$

it can be seen that F_1° is the molar free energy of the pure liquid. If the molecular weight employed is that in the vapour phase, we have by (125),

$$\overline{F}_1 = F_1^{\circ} + RT \log p_1/p_1^{\circ},$$

or $a_1 = p_1/p_1^{\circ}$. Now Raoult's Law (131), can be written as

$$p_1/p_1^{\circ} = \frac{n_1}{n_1 + n_2} = N_1.$$

If the molecular weights are chosen according to the principles given above this holds accurately for very small concentrations of the solute. In some solutions it has been found experimentally to hold over a considerable concentration range. In such a case it is evident that $\bar{F}_1 = F^{\circ}_1 + RT \log N_1$.

This equation is often taken as representing the behaviour of an "ideal" solution. The ratio $f_1 = a_1/N_1$, which is obviously unity in the pure liquid, is the activity coefficient and may be taken as a measure of the deviation from the ideal behaviour.

(3) Relation between activities determined by conventions (1) and (2). When a complete range of solutions exists which extends from one pure liquid to the other, either convention may be adopted. It is of interest to compare the results of the two definitions. Consider the component S_2 . According to the second definition, i.e. taking the activity as unity in the pure liquid S_2 , the partial free energy in any given solution, since $a_2 = f_2 N_2$, is

$$\bar{F}_2 = F_2^{\circ} + RT \log f_2 N_2.$$

Jules Lee every ... " care

In the same solution, by the first definition, we have

$$\bar{F}_2 = (F_2^{\circ})' + RT \log f_2' N_2,$$

where $f_2' = 1$, when N_2 is very small. Comparing these equations it is evident that

$$(\bar{F}_{2}^{\circ})' - F_{2}^{\circ} = RT \log f_{2}/f_{2}'.$$
(133)

If the solution is so dilute that $f_2' = 1$, we may distinguish f_2 as f_2 °, and we have then

$$(\bar{F}_{2}^{\circ})' - F_{2}^{\circ} = RT \log f_{2}^{\circ}. \dots (134)$$

Thus if the activity coefficient is taken as unity in the pure liquid and f_2° is its value in an extremely dilute solution in another solvent, $RT \log f_2^{\circ}$ is equal to the difference between the standard free energy for dilute solutions of S_2 in the given solvent and its free energy in the pure liquid state.

> Activity Coefficients of Alcohols in Aqueous Solution. We will illustrate these relations by reference to aqueous solutions of some of the aliphatic alcohols. There is no great difficulty in the direct determination of the partial vapour pressures of solutions of the lower alcohols. If p_2 is the pressure of the alcohol over a given solution, p_2 ° the pressure of the pure alcohol at the same temperature, taking the activity of the alcohol as unity in the pure liquid, we have

$$a_2 = p_2/p_2^{\circ}$$
; $f_2 = p_2/p_2^{\circ}N_2$.

The activities and activity coefficients (shown for convenience as $\log f_2$) of some of the lower aliphatic alcohols in aqueous solution, as determined in this way, are shown in Figs. 9 and 10. It is obviously a simple matter to extrapolate these curves to $N_2 = 0$, and thus obtain f_2 °, the activity coefficient of the alcohol, on the basis of this definition, in a very dilute aqueous solution. The values obtained are given in Table VI.* By (134) $RT \log f_2^{\circ}$ is the difference between F_2° , the free energy

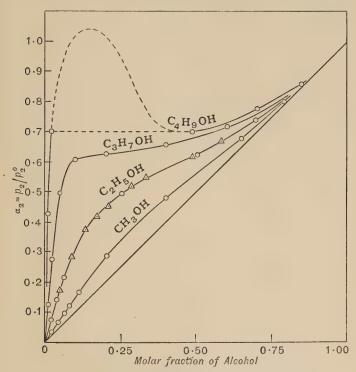


Fig. 9.—Activities of aliphatic alcohols at 25° in aqueous solutions.

of the pure liquid alcohol, and $(\bar{F}^{\circ}_{\ 2})'$ its standard free energy in water as obtained by

$$\overline{F}_2 = (\overline{F}^{\circ}_2)' + RT \log \alpha_2,$$

^{*} Butler, Thomson and Maclennan, J. Chem. Soc., p. 674, 1933.

when the activity is made equal to N_2 in very dilute solutions.

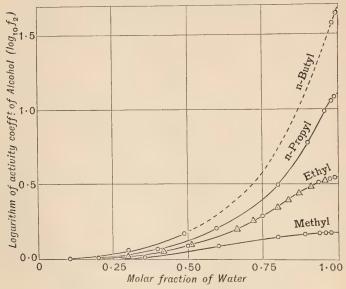


Fig. 10.—Activity coefficients of alcohols in aqueous solutions.

TABLE VI.

ACTIVITY COEFFICIENTS AND STANDARD FREE ENERGIES OF ALIPHATIC ALCOHOLS IN DILUTE AQUEOUS SOLUTION.

	f 2°.	$F^{\circ}{}_{2}{}' - F^{\circ}{}_{2}.$		f_2° .	$F^{\circ}{}_{2}{}' - F^{\circ}{}_{2}.$
Methyl Ethyl n-Propyl n-Butyl	$ \begin{array}{r} 1.51 \\ 3.48 \\ 12.5 \\ 46.5 \end{array} $	$egin{array}{c} 240 \\ 740 \\ 1500 \\ 2280 \\ \end{array}$	n-Amyl* n-Hexyl* n-Heptyl* n-Octyl*	219 903 3560 12300	3190 4030 4850 5580

^{*} In these cases f_2° is taken as $1/N_2$.

n-Butyl alcohol is not miscible in water in all proportions, and consequently there is a considerable range of solutions which is not accessible to measurements. Nevertheless outside the limits of immiscibility the methods given above can be applied. Vapour pressure determinations become increasingly difficult for the higher alcohols, but the activity coefficients in dilute aqueous solution can be determined approximately from the solubility in water in the following way.

When two phases are in equilibrium with each other the partial free energy of every component which is common to the two phases must be the same in each. Take, say, heptyl alcohol. If sufficient of the alcohol is shaken with water, two layers are obtained. Let the molar fraction of the alcohol in the alcohol-rich layer be N_2 , and in the aqueous layer N_2' . If \bar{F}_2 , \bar{F}_2' , a_2 , a_2' and f_2 , f_2' are the partial free energies, activities and activity coefficients in the two layers, and defining the activity as unity in the pure alcohol, we have

or since for equilibrium, $\bar{F}_2 = \bar{F}_2$, we have

$$a_2 = a_2', \quad \text{or} \quad f_2 N_2 = f_2' N_2'.$$

Thus $f_2 = f_2' N_2' / N_2$. If the alcohol-rich layer contains only a small proportion of water we shall be making no very great error if we take the activity of alcohol in it, $a_2' = f_2' N_2'$, as unity. Then we have $f_2 = 1/N_2$. If the proportion of alcohol in the aqueous layer is small this may also be taken as equal to the limiting value f_2° . f_2° is thus approximately equal to the reciprocal of the molar fraction of alcohol in the saturated aqueous solu-

tion. The values of f_2° for dilute solutions of some of the higher alcohols as determined in this way are given in Table VI.

Activity of a Solute from the Vapour Pressures of the Solvent. When the activity of one component of a binary solution is known over a range of concentration the variation of the activity of the second component over the same range can be found by the application of the Duhem-Margules equation. Putting

$$d\bar{F}_1 = RT \;.\; d\log\,a_1,\; d\bar{F}_2 = RT \;.\; d\log\,a_2,$$
 in (118), we have

$$n_1$$
 . $d \log a_1 + n_2$. $d \log a_2 = 0$,(135)

and since it can easily be shown that

can easily be shown that
$$n_1 \cdot d \log N_1 + n_2 \cdot d \log N_2 = 0$$
;

it follows that

$$n_1$$
, $d \log f_1 + n_2$, $d \log f_2 = 0$(136)

Therefore, integrating from the values for a solution A to those for a solution B:

$$(\log \alpha_2)_B - (\log \alpha_2)_A = -\int_A^B \frac{n_1}{n_2} \cdot d \log \alpha_1 ; \dots (137)$$

and
$$(\log f_2)_B - (\log f_2)_A = -\int_A^B \frac{n_1}{n_2} \cdot d \log f_1.$$
 ...(138)

The variation of α_2 (or f_2) between any two solutions can thus be found if a_1 (or f_1) is known as a function of the molar ratio (n_1/n_2) between these limits. activity of an involatile solute can be determined in this way from the partial vapour pressure of the solvent. In some cases these equations can be conveniently integrated graphically by plotting n_1/n_2 against $\log \alpha_1$ or $\log f_1$. When the range over which the integration is to be made includes the pure solvent $(n_1/n_2 = \infty)$ difficulties arise, and it is better to make use of some empirical relation between n_1/n_2 and α_1 (or f_1) for dilute solutions.

The following table shows the activity coefficients of cane sugar in aqueous solutions at 50° as determined from the partial vapour pressures of water in this way.* In this case the solution remains practically ideal up to $n_2/n_1 = 0.014$, and no difficulty arises over the extrapolation to infinite dilution.

n_2/n_1 .	N_1 .	$f_1 = p_1/p_1^{\circ} N_1.$	N_2 .	$f_2 = a_2/N_2$
0.005993	0.9940	0.9999	0.0060	1.000
0.01382	0.9864	1.0071	0.0136	1.000
0.01773	0.9826	0.9974	0.0174	1.134
0.02435	0.9762	0.9933	0.0238	1.269
0.03472	0.9665	0.9950	0.0335	1.437
0.04615	0.9559	0.9914	0.0441	1.624
0.05939	0.9439	0.9852	0.0561	1.847
0.07259	0.9323	0.9699	0.0677	2.053
0.09906	0.9098	0.9626	0.0902	2.427
0.1222	0.8911	0.9347	0.1089	2.801

Variation of the Partial Free Energy with Temperature and Pressure. Let F be the free energy of a solution containing n_1 mols of S_1 , n_2 mols of S_2 , etc. By definition F = E - TS + pv.

Differentiating with respect to n_1 , we have

$$\frac{\partial F}{\partial n_1} = \frac{\partial E}{\partial n_1} - T \frac{\partial S}{\partial n_1} + p \frac{\partial v}{\partial n_1},$$
or
$$\bar{F}_1 = \bar{E}_1 - T \bar{S}_1 + p \bar{v}_1 = \bar{H}_1 - T \bar{S}_1, \dots (139)$$

^{*} Perman, Trans. Faraday Soc., 24, 330, 1928.

where $\bar{S}_1 = (dS/dn_1)_{t,\,p,\,n_2}$ etc., is the partial molar entropy defined in the same way as the partial molar energy or volume, etc. We can now find the change of \bar{F}_1 with temperature and pressure.

First differentiating F with respect to T, we have

by (43), $\left(\frac{dF}{dT}\right)_{p,\,n} = -S,$

and differentiating again with respect to n_1 ,

$$\begin{split} \left(\frac{d^2F}{dT\cdot dn_1}\right)_{\mathcal{D}} &= -\frac{dS}{dn_1} = -\bar{S}_1.\\ \left(\frac{d^2F}{dT\cdot dn_1}\right)_{\mathcal{D}} &= \frac{d^2F}{dn_4\cdot dT} = \frac{d\bar{F}_1}{dT}\,, \end{split}$$

Since

and introducing the value of \bar{S}_1 given by (139), we have

$$\frac{d\bar{F}_1}{dT} = -\bar{S}_1 = \frac{\bar{F}_1 - \bar{H}_1}{T}.$$
 (140)

Dividing through by T, we thus find

$$\frac{\mathcal{T}_{d\bar{F}_{1}} - \bar{F}_{1} \cdot dT}{\mathcal{T}_{2} \cdot dT} = \frac{1}{T} \cdot \frac{d\bar{F}_{1}}{dT} - \frac{\bar{F}_{1}}{T^{2}} = -\frac{\bar{H}_{1}}{T^{2}},$$

$$\frac{d(\bar{F}_{1}/T)}{dT} = -\frac{\bar{H}_{1}}{T^{2}}. \qquad (141)$$

Similarly differentiating F with respect to p, we have by (44),

$$\left(\frac{dF}{dp}\right)_{t,n} = v,$$
and
$$\left(\frac{d^2F}{dp \cdot dn_1}\right)_{t,n_2,\text{ etc.}} = \frac{dv}{dn_1} = \bar{v}_1.$$
Since
$$\frac{d^2F}{dp \cdot dn_1} = \frac{d^2F}{dn_1 \cdot dp} = \frac{d\bar{F}_1}{dp},$$
we have
$$\frac{d\bar{F}_1}{dp} = \bar{v}_1. \qquad (142)$$

i.e. the rate of change of the partial free energy of a component with the pressure is equal to its partial volume.

Determination of Activity from the Freezing Point of Solutions. Consider an aqueous solution containing n_1 mols of water (S_1) and n_2 mols of a solute S_2 . The partial molar free energy in (1) pure water, (2) ice, (3) the solution at the freezing point of pure water (t_0) and at the freezing point of the solution (t) are represented by the symbols given below.

The conditions for the equilibrium of ice and water at its freezing point (t_0) , and of ice and the solution at its freezing point (t) are given by the equalities in this scheme.

The variation of the free energy of ice with the temperature, according to (141), is

$$\frac{d(F_s/t)}{dt} = -\frac{H_s}{t^2},$$

where H_s is the molar heat content of ice. Integrating this equation between t and t_0 , we have

$$(F_s)_{t_0}/t_0 - (F_s)_t/t = -\int_t^{t_0} H_s/t^2 \cdot dt.$$

The variation of \bar{F}_1 between the same temperatures is similarly given by

$$\frac{(\bar{F}_1)_{t_0}}{t_0} - \frac{(\bar{F}_1)_t}{t} = - \int_t^{t_0} \!\! \frac{\bar{H}_1}{t^2} \, . \, dt,$$

where \bar{H}_1 is the partial molar heat content of water in the solution. Combining these equations and writing $(F_s)_t = (\bar{F}_1)_t$, it follows that

$$\frac{(\bar{F}_1)_{t_0} - (F_s)_{t_0}}{t_0} = -\int_t^{t_0} \frac{\bar{H}_1 - H_s}{t^2} \cdot dt,$$

and since $(F_s)_{t_0} = (F_1^{\circ})_{t_0}$, and by the definition of the activity of the solvent

 $(\bar{F}_1)_{t_0} = (F^{\circ}_1)_{t_0} + Rt_0 \log(\alpha_1)_{t_0},$ we have $\log(\alpha_1)_{t_0} = -\int_t^{t_0} \frac{\bar{H}_1 - H_s}{Rt^2} \cdot dt. \quad \dots (143)$

If the solution is so dilute, or its nature is such that the partial heat of water in the solution is negligible, instead of \tilde{H}_1 we may write H°_1 (i.e. the partial heat content of water in the solution is replaced by the heat content of pure water). $\Delta H = H^{\circ}_1 - H_s$ is the latent heat of fusion of ice, the variation of which over a considerable range of temperature may be expressed by the Kirchoff equation $\Delta H = \Delta H_0 + \Delta C_n(t_0 - t)$,

where ΔC_p is the difference between the molar heat capacities of ice and water, and ΔH_0 the latent heat of fusion of ice at t_0 . According to Lewis and Randall these quantities have the values

 $\Delta H_0 = 1438$ calories, $\Delta C_p = -9$ calories.

Introducing these values into (143), we have *

$$(\log a_1)_{t_0} = -\int_t^{t_0} \frac{1438 - 9(t_0 - t)}{Rt^2} \cdot dt.$$

*The steps of this calculation are: writing $t^2 = t_0^2 - 2t_0\Delta t + (\Delta t)^2$, and neglecting $(\Delta t)^2$, we have to a first approximation

$$\begin{split} \frac{1438 - 9\Delta t}{Rt^2} &= \frac{1}{Rt_0^2} \left\{ (1438 - 9\Delta t) \left(1 + \frac{2t_0\Delta t}{t_0^2} \right) \right\} \\ &= \frac{1}{Rt_0^2} \left\{ 1438 + \left(\frac{2 \times 1438}{t_0} - 9 \right) \Delta t. \end{split}$$

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Writing $t = t_0 - \Delta t$, we obtain

$$\frac{1438 - 9(t_0 - t)}{Rt^2} = 0.009696 + 0.0000103\Delta t,$$

and
$$(\log a_1)_{t_0} = -0.009696\Delta t - \frac{0.0000103\Delta t^2}{2}$$
...(144)

This gives the activity of the solvent at its freezing point as a function of the freezing point depression. In order to find the activity of the solute we can use the expression $d \log a_2 = -(n_1/n_2)d \log a_1$. If the solution contain m mols of the solute in 1000 gms. (55·51 mols) of water, we have

$$d \log(\alpha_2)_{t_0} = \frac{0.009696 \times 55.51}{m} \cdot d(\Delta t) + \frac{0.0000051 \times 55.51}{m} \cdot 2\Delta t \cdot d(\Delta t) \cdot \dots (145)$$

For a very dilute solution we can neglect the second term of this equation, and putting in that case $a_2 = m$,* we obtain

$$\frac{d(\Delta t)}{dm} = \frac{1}{0.009696 \times 55.51} = 1.858.$$

This is the molecular lowering of the freezing point for very dilute solutions. Representing it by λ , (145) becomes

$$d \log (a_2)_{t_0} = \frac{d(\Delta t)}{\lambda m} + 0.00057 \frac{\Delta t \cdot d(\Delta t)}{m}.$$
 ...(146)

In order to integrate this it is necessary to resort to graphical methods.

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^{*} Note that the correct choice of the molecular weight comes in at this point.

* Integration formulae. In order to integrate this expression, Lewis and Randall make use of the quantity j, which is defined by

$$\frac{\Delta t}{\lambda m} = 1 - j$$
, or $j = 1 - \frac{\Delta t}{\lambda m}$.

Since at infinite dilution $\Delta t/m$ is equal to λ , j is a measure of the difference between the actual molecular depression of the solution and the value at infinite dilution. By differentiation, we have

$$rac{d(\Delta t)}{\lambda m}-rac{\Delta t\cdot dm}{\lambda m^2}=-dj$$
 ,

and

$$\frac{d(\Delta t)}{\lambda m} = (1-j)\frac{dm}{m} - dj = (1-j)^{4}\log m - dj.$$

Introducing this value into (146), it follows that

 $d \log (a_2)_{t_0} = (1-j) d \log m - dj + 0.00057 \cdot \frac{\Delta t}{m} \cdot d(\Delta t),$ and therefore,

$$\log \frac{(a_2)_{t_0}}{m} = -\int_0^m j \cdot d \log m - j + \int_0^m 0.00057 \cdot \frac{\Delta t}{m} \cdot d(\Delta t).$$

The first integral $A = \int_0^m \frac{j}{m} \cdot dm$ can be obtained by

plotting j/m against m and taking the area of the curve from 0 to m, the second B by plotting $\Delta t/m$ against Δt , and multiplying by 0.00057.

The following data for solutions of butyl alcohol in water, obtained by Harkins and Wampler,* illustrate this procedure. Table VIII gives the values of m, Δt , $\Delta t/m$, j and j/m for some of the solutions.

^{*} J. Amer. Chem. Soc., 53, 850, 1931.

TABLE VIII.

FREEZING POINT DEPRESSIONS OF BUTYL ALCOHOL SOLUTIONS.

m.	Δt .	$\Delta t/m$.	ĵ.	j/m (Interpolated)
0.004134	0.007669	1.855	0.00201	0.487
0.01140	0.02112	1.851	0.00525	0.460
0.01605	0.02957	1.842	0.00711	0.443
0.02420	0.04452	1.840	0.00997	0.412
0.04631	0.08470	1.829	0.01572	0.339
0.05206	0.09505	1.826	0.0174	0.325
0.06894	0.1255	1.821	0.0197	0.286
0.09748	0.1768	1.814	0.0238	0.245
0.1641	0.2956	1.801	0.0306	0.1864
0.2153	0.3863	1.794	0.0343	0.1593
0.4197	0.7442	1.773	0.0455	0.1084
0.7035	1.2310	1.750	0.0583	0.0804

Fig. 11 shows j/m plotted against m. A certain latitude in drawing the curve to zero concentration is obviously

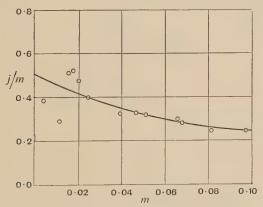


Fig. 11.—j/m for butyl alcohol solutions plotted against m.

possible, but this makes very little difference to the result. The values of the integrals A and B and of a_2/m , obtained from the smoothed curves for round concentrations are given in Table IX.

TABLE IX.

m.	-A.	В.	a_2/m_2 .
0.001	.000499		0.9990
$\cdot 003$	001485		0.9971
.006	-002946		0.9942
.010	.004840	0.00001	0.9906
.020	0.009308	-00004	0.9823
.040	0.001710	-00008	0.9691
.070	0.02661	-00013	0.9546
.100	0.03442	.00019	0.9433
·200	0.05420	-00038	0.9161
.300	0.06991	.00054	0.8974
-400	0.08201	-00071	0.8817
•500	0.09252	.00089	0.8681
.600	0.1019	.00106	0.8563
.700	0.1104	.00123	0.8465

Change of Activity with Temperature. If the activity of a component in a given solution is defined by

$$\bar{F}_1 = \bar{F}^{\circ}_{1} + RT \cdot \log \alpha_1$$

where a_1 is fixed by any of the conventions mentioned above, we have

$$\log \alpha_{1} = \frac{\overline{F}_{1}}{R\overline{T}} - \frac{\overline{F}_{1}}{R\overline{T}}, \frac{2 \log \alpha_{1}}{d \overline{T}} = \frac{d \overline{F}_{1}}{d \overline{T}} = \frac{d \overline{F}_{1}}{d \overline{T}}.$$
(141),

and therefore, by (141),

$$\frac{d \log a_1}{dT} = -\frac{\bar{H}_1}{RT^2} + \frac{\bar{H}_1^{\circ}}{RT^2} = -\frac{\bar{L}_1}{RT^2}, \dots (147)$$

where \bar{H}_1 , \bar{H}°_1 are the partial heat contents of the component in the given solution and in the standard state to which \bar{F}°_1 refers, and $\bar{L}_1 = \bar{H}_1 - \bar{H}^{\circ}_1$ is the heat content

relative to this standard state. The change of activity (and also of the activity coefficient, if the composition is expressed in a way which does not depend on the temperature) over a range of temperature can be obtained by integrating this equation. For a wide range of temperature it may be necessary to give \bar{L}_1 as a function of the temperature as in Kirchoff's equation.

not neglected.

Activity from the freezing point when heat of dilution is to neglected. As before, (143), we have
$$\log (a_1)_{t_0} = -\int_t^{t_0} \frac{\bar{H}_1 - H_s}{Rt^2} \, dt,$$

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but we cannot now identify \bar{H}_1 with H_1° . Adding and

$$\log (a_1)_{t_0} = -\int_t^{t_0} \frac{\bar{H}_1 - H^\circ_1}{Rt^2} dt - \int_t^{t_0} \frac{H^\circ_1 - H^\circ_2}{Rt^2} dt, \text{ define two.} \text{ letters } t$$

$$(147) \text{ this becomes}$$

but by (147), this becomes

$$\log (a_1)_{t_0} = \widetilde{\log (a_1)_{t_0}} - \widetilde{\log (a_1)_t} - \int_t^{t_0} \frac{H^\circ_1 - H_s}{Rt^2} \cdot dt.$$

Therefore

$$\log\left(a_{1}\right)_{t} = -\int_{t}^{t_{0}} \frac{H^{\circ}_{1} - H_{s}}{Rt^{2}} \cdot dt. \dots \dots (148)$$

This integral thus really gives the activity of the solvent at the freezing point of the solution (t). This is equal to the activity at t_0 only when, as was previously supposed to be the case, the heat of dilution of the solution is negligible. When this is not so, the activity at any given temperature can be obtained by adding to the value of (148), the change of activity between t and the given temperature as determined by the integral of (147). This involves a knowledge of the relative heat contents of the solutions, and if the temperature interval is large, possibly also their variation with temperature.

*Solubility of Solids. Let F_s be the molar free energy of a solid, and \bar{F}_2 its partial free energy in a saturated solution in a given solvent. The condition of equilibrium is $F_s = \bar{F}_2$. Writing $\bar{F}_2 = \bar{F}_2^\circ + RT$. log $m_2 f_2$, we have

$$\frac{F_s - \bar{F}^{\circ}_2}{RT} - \log f_2 = \log m_2,$$

and, differentiating with respect to the temperature, we obtain

$$-\frac{H_s-\bar{H}^\circ{}_2}{R\,T^2} - \left(\frac{d\,\log f_2}{d\,T}\right)_m - \left(\frac{d\,\log f_2}{dm_2}\right)_T \cdot \frac{dm_2}{d\,T} = \frac{d\,\log\,m_2}{d\,T}\,,$$

or, since by (147),

$$\left(rac{d\,\log f_2}{d\,T}
ight)_m = -rac{ar{H}_2 - ar{H}^\circ_{\,\,2}}{R\,T^2}$$
 ,

this becomes

$$\frac{\bar{H}_2-H_s}{RT^2}\!=\!\!\left(\!\frac{d\,\log f_2}{dm_2}\!\right)_T\!\cdot\!\frac{dm_2}{dT}\!+\!\frac{d\,\log\,m_2}{dT}\!\cdot\!$$

The variation of the activity coefficient of nonelectrolytes with the concentration is probably often so small that the first term on the right can be neglected, and we then have

$$\frac{d \log m_2}{dT} = \frac{\bar{H}_2 - H_s}{RT^2}, \quad \dots (149)$$

where $\bar{H}_2 - H_s$ is the partial heat of solution in the saturated solution.

Example. In the case of solutions of salts the term $(d \log f_2/dm_2)_T$ cannot safely be neglected. The heat of solution of slightly soluble salts can be determined in the following way. In Part I (p. 174) it is shown how the reciprocals of the solubility products of a slightly soluble salt can be extrapolated to give an ideal value for the solu-

bility product in an infinitely dilute solution (i.e. activity coefficient unity). (149) can be applied to the values so obtained to give the heat of solution of the salt at infinite dilution. Butler and Hiscocks found (J. Chem. Soc., 2554, 1926) that for thallous chloride the values of $1/\sqrt{m_{\rm Tl}}^{\circ}$. $m_{\rm Cl}^{\circ}$ at infinite dilution were 0°, 163.6; 25° , 72.1. The heat of solution of the salt as determined by $\frac{d \log (m_{\rm Tl} \circ m_{\rm Cl})}{dT} = \frac{\Delta H^{\circ}}{RT^2}$ (since there are two ions), over this range of temperatures is thus $\Delta H = 10560$ calories.

*The Osmotic Pressure of Solutions. When two phases are separated by a membrane which offers no resistance to the passage of one component and is completely impermeable to all others, the condition of equilibrium is that the partial free energy of the component which can pass freely through the membrane shall be the same in both phases, but there is no such condition for the components which cannot pass the membrane.

Consider a solution of a solute S_2 in a solvent S_1 , separated from the solvent by a membrane which is permeable to S_1 only. Let the partial free energy of S_1 at the temperature T and the pressure P_0 be $(F^{\circ}_{1})_{P_0}$ in the pure solvent and $(\bar{F}_{1})_{P_0}$ in the solution. If the pressure on the solvent has the constant value P_0 , it is necessary in order to establish equilibrium across the membrane to increase the pressure on the solution until the partial free energy of the solvent in the latter is equal to $(\bar{F}_{1})_{P_0}$. The variation of \bar{F}_1 with pressure is given according to (142) by

$$d\bar{F}_1 = \bar{v}_1 dP$$
.

Integrating this between the pressures P_0 and P, we have

$$(\bar{F}_1)_P - (\bar{F}_1)_{P_0} = \int_{P_0}^P \tilde{v}_1 \cdot dP. \dots (150)$$

We have to find the pressure which is required to make $(\bar{F}_1)_P$ equal to $(F^{\circ}_1)_{P_0}$. Writing

$$(F_1^{\circ})_{P_0} - (\bar{F}_1)_{P_0} = -RT \log \alpha_1,$$

(150) may therefore be replaced by

$$RT \log a_1 = -\int_{P_0}^{P} \vec{v}_1 \cdot dP$$
.(151)

If \bar{v}_1 is taken as constant and independent of the pressure between P and P_0 , we obtain by integration,

$$RT \log a_1 = -\bar{v}_1(P - P_0) \dots (152)$$

where $P - P_0$ is the osmotic pressure.

The following table gives a comparison between the osmotic pressures of aqueous solutions of cane sugar and a-methyl glucoside at 0° , and the values calculated by this equation, taking for \bar{v}_1 a mean value between P_0 and P.* The activities of water in the solutions were obtained from its partial vapour pressures as $a_1 = p_1/p_1^{\circ}$.

TABLE X.
CANE SUGAR.

$egin{array}{lll} { m concentration} & & & & & & \\ { m ms. Sugar in} & & & & & & \\ 100 { m gms.} & & & & & & \\ { m Water.} & & & & & & \\ \end{array}$		\tilde{v}_1 . (per gram.)	$P-P_0$. (cale,)	$P-P_0$. (obs.).	
56.50	0.03516	0.99515	43.91	43.84	
81.20	0.05380	0.99157	$67 \cdot 43$	67.68	
112.00	0.07983	0.98690	100.53	100.43	
141.00	0.10669	0.98321	$134 \cdot 86$	134.71	
	a-ME	ETHYL GLUCO	SIDE.		
35.00	0.03878	0.99810	48.29	48.11	
45.00	0.05153	0.99709	64.22	63.96	
55.00	0.06451	0.99579	80.50	81.00	
64.00	0.09253	0.99254	115.74	115.92	

^{*} Berkeley, Hartley and Burton, Phil. Trans., 218, 295, 1919; Proc. Roy. Soc., A, 92, 483, 1916.

It is obvious that in a precise calculation of the osmotic pressure the variation of the partial volume of the solvent \bar{v}_1 with the pressure ought to be taken into account. Perman and Urry * have expressed \bar{v}_1 as a linear function of $P - P_0$ by the equation

$$\bar{v}_1 = \bar{v}_1^{\circ} (1 - s(P - P_0)).$$

Then (151) becomes

$$\begin{split} RT \log a_1 &= -\int_{P_0}^P \tilde{v}_1{}^\circ [1 - s(P - P_0)] \cdot dP \\ &= - \hat{v}_1{}^\circ (P - P_0) \left(1 - \frac{s(P - P_0)}{2}\right). \quad ...(153) \end{split}$$

where the relatively small term sP_0^2 is neglected.

Table XI gives a comparison of the observed osmotic pressures of a cane sugar solution containing 1 gm. mol sugar in 1000 gms. water, at a few temperatures, with the values calculated by (152), a_1 being determined from the partial vapour pressures by $a_1 = p_1/p_1^{\circ}$ (s is about 370×10^{-7}).

TABLE XI.

OBSERVED AND CALCULATED OSMOTIC PRESSURES OF
A SUCROSE SOLUTION.

Temperature.	$-\log_e a_1$.	v_1 °.	$P-P_0$. (Calc.).	$P-P_0$. (Obs.).
40° 50° 60° 70° 80°	0.01940 0.01914 0.01839 0.01848 0.01809	$\begin{array}{c} 1.006456 \\ 1.010650 \\ 1.016843 \\ 1.0195 \\ 1.0257 \end{array}$	$ \begin{array}{c} 27.51 \\ 27.88 \\ 27.45 \\ 28.34 \\ 28.41 \end{array} $	27·70 28·21 28·37 28·62 28·82

^{*} Proc. Roy. Soc., A, 126, 44, 1930.

Examples.

- 1. Derive van't Hoff's law for the osmotic pressures of dilute solutions (pv = RT) from (129a).
- 2. The following are the measured partial pressures of solutions of water (S_1) and propyl alcohol (S_2) at 25° :

N_2	p_1	p_2	N_2	p_1	p_1
0	23.8	0.0	0.6	19.9	15.5
0.05	$23 \cdot 2$	10.8	0.8	13.4	17.8
$0 \cdot 1$	$22 \cdot 7$	$13 \cdot 2$	0.9	$8 \cdot 1$	19.4
0.2	21.8	13.6	0.95	$4 \cdot 2$	20.8
0.4	21.7	$14 \cdot 2$	1.00	0.0	21.8

Find (1) the activities, (2) the partial free energies of water and alcohol, taking the partial free energies as zero in the pure liquids. Find also by (117) the total free energies of the solutions on the same basis and plot against N_2 .

- 3. The solubility of carbon tetrachloride in water at 20° C. is 0.080 gms. CCl_4 to 100 gms. H_2O . Assuming that carbon tetrachloride dissolves practically no water, and that its activity coefficient is 1 in the pure liquid, find its activity coefficient in the saturated aqueous solution. (10600.)
- 4. According to Bell (J. Chem. Soc., 1932, p. 2907), the equilibrium molar fraction of water in chlorobenzene, when shaken with Na_2SO_4 , $10H_2O$ and Na_2SO_4 is nearly 0.02 at 25°. The dissociation pressure of the salt hydrate is 19.2 mm. and that of pure water 23.8 mm. at 25° . Find the activity coefficient of water in the chlorobenzene solution. (42.)

CHAPTER VI

ACTIVITY COEFFICIENTS AND RELATED PROPERTIES OF STRONG ELECTROLYTES

Activity and Activity Coefficient of Strong Electrolytes. A strong electrolyte, such as sodium chloride in aqueous solution, is regarded as being largely dissociated because its effect on the partial free energy of the water (and therefore on the freezing point, osmotic pressure and similar properties of the solution) is approximately twice that of the same number of molecules of a neutral substance. In very dilute solutions the change of the free energy of water becomes in fact exactly twice that produced by an equal number of molecules of, say, sugar, and in such a case we are justified in regarding the salt as completely dissociated.

Consider the salt AB which dissociates as

$$AB = A^+ + B^-.$$

Let \bar{F}_+ , \bar{F}_- , \bar{F} be the partial molar free energies of A^+ , B^- and AB in the solution. We can define the activities of the ions by

 $\bar{F}_{+} = \bar{F}^{\circ}_{+} + RT \log \alpha_{+}, \\ \bar{F}_{-} = \bar{F}^{\circ}_{-} + RT \log \alpha_{-},$ (154)

and since in dilute solutions each ion produces the same change of the free energy of the solvent as a separate

molecule, it is possible to adopt the conventions that $a_+ = m_+$ and $a_- = m_-$, when m_+ (or m_-) = 0, where m_+ , m_- are the concentrations of the ions. We may also write

$$\bar{F} = \bar{F}^{\circ} + RT \log \alpha, \dots (155)$$

where α is the activity of the salt, AB, but since a molecule of the salt does not cause the theoretical molecular lowering of the partial free energy of the solvent, it is not possible to identify α with m in very dilute solutions.

. The partial free energy of a gram molecule of the salt AB must be the sum of the molar free energies of A^+ and B^- (see p. 80), or $\bar{F} = \bar{F}_+ + \bar{F}_-$,* and therefore

$$\bar{F}^{\circ} + RT \log \alpha = \bar{F}^{\circ}_{+} + \bar{F}^{\circ}_{-} + RT \log \alpha_{+}\alpha_{-}.$$

If the activity of the salt is so defined that $\bar{F}^\circ = \bar{F}^\circ_+ + \bar{F}^\circ_-$ we have then

$$\alpha = \alpha_{+}\alpha_{-}$$

and writing $a_{\pm} = \sqrt{a_{+}a_{-}}$, it follows that

$$\bar{F} = \bar{F}^{\circ} + 2RT \log \alpha \pm \dots \tag{156}$$

 $a \pm is$ called the mean activity of the salt.

The activity coefficients of the ions are $f_+ = \alpha_+/m_+$ and $f_- = \alpha_-/m_-$, and by definition they obviously become equal to unity in very dilute solutions. If we took the activity coefficient of the salt as the ratio of its activity to its concentration, i.e. $f = \alpha/m = \alpha_+\alpha_-/m$, we should obviously obtain a quantity which cannot become equal to unity at small concentrations. If, however, we write

$$f_{\pm} = \alpha_{\pm}/m_{\pm} = \sqrt{f_{\pm}f_{-}},$$

^{*} This also follows from the consideration that the partial free energy of the salt must be the same whether we regard it as the component AB, or as the components A_+ , B_- .

where $m_{\pm} = \sqrt{m_{+}m_{-}}$, we obtain a quantity called the mean activity coefficient which evidently becomes equal to unity when f_{+} and f_{-} are unity.

In solutions of strong electrolytes, which are certainly very largely dissociated, it is usual to take m_+ , m_- as the total stoichiometrical concentration of the ions, without having regard to the degree of dissociation of the salt. Thus in a sodium chloride solution, m_{Na^+} , m_{Cl} are taken as the total concentrations of sodium and chloride in the solution, without distinguishing to what extent they are present as ions or as undissociated molecules. The activity coefficient obtained in this way has been called the stoichiometrical activity coefficient.

The activity of other types of electrolytes can be similarly defined. Suppose we have a salt $A_{\nu_1}B_{\nu_2}$ which dissociates into ν_1 ions A and ν_2 ions B, as in the equation

$$A_{\nu_1}B_{\nu_2} = \nu_1A^+ + \nu_2B^-.$$

The partial molar free energies of the ions are given by (154) as before, and the partial molar free energy of the salt is equal to

 $\boldsymbol{\bar{F}} = \boldsymbol{v}_1 \boldsymbol{\bar{F}}_1 + \boldsymbol{v}_2 \boldsymbol{\bar{F}}_2,$

so that if the activity of the salt is defined by

$$\bar{F} = \bar{F}^{\circ} + RT \log \alpha, \quad \dots (157)$$

where $\bar{F}^{\circ} = \nu_1 \bar{F}_1^{\circ} + \nu_2 \bar{F}_2^{\circ}$, we have

or

$$\log \alpha = \nu_1 \log \alpha_+ + \nu_2 \log \alpha_-,$$

 $\alpha = \alpha_+^{\nu_1} \alpha_-^{\nu_3}.$ (158)

The mean activity of the salt is defined as

$$a_{\pm} = (a_{+}^{\nu_{1}} a_{-}^{\nu_{2}})^{\nu_{1} + \nu_{2}}, \dots (159)$$

and the mean activity coefficient as

where

or

$$f_{\pm} = \alpha_{\pm}/m_{\pm},$$

 $m_{\pm} = (m_{+}^{\nu_{1}} \cdot m_{-}^{\nu_{2}})^{1/\nu_{1} + \nu_{2}},$

 f_{\pm} obviously becomes unity when

$$f_1 = \alpha_+/m_+$$
 and $f_2 = \alpha_-/m_-$

become unity. Finally, comparing (157) and (158), it can be seen that

 $\bar{F} = \bar{F}^{\circ} + (\nu_1 + \nu_2)RT \log \alpha_{\pm}.$ (160)

The more important methods for the determination of activity coefficients, which can be applied with only slight modification to solutions of electrolytes, have already been described. As an illustration of the determination of the activity coefficient of an electrolyte from the partial free energy of the solvent, consider a solution containing n_1 mols of the solvent and n_2 mols of a salt a molecule of which dissociates into ν_1 positive and ν_2 negative ions. If \bar{F}_1 , \bar{F}_2 are the partial molar free energies of the solvent and salt in the given solution, we have by (118),

 $dar{F}_2 = -n_1/n_2$. $dar{F}_1$,

or writing $\bar{F}_2 = \bar{F}_2^{\circ} + RT$. $\log a_2$, where a_2 is the activity of the salt as defined by (157), we have

$$RT \cdot d(\log a_2) = -n_1/n_2 \cdot d\bar{F}_1.$$

Instead of $\log a_2$ we may use $(\nu_1 + \nu_2) \log a_{\pm}$, and we then have for the mean activity of the salt,

$$d(\log a_{\pm}) = -\frac{1}{(\nu_1 + \nu_2)RT} \int \frac{\overline{n_1}}{n_2} d\overline{F_1},$$

$$d(\log a_{\pm}) = -\frac{1}{(\nu_1 + \nu_2)} \int \frac{n_1}{n_2} d\log a_1. \dots (161)$$

Similarly it is easy to obtain a corresponding equation for the activity coefficient (see 138), viz.:

$$d(\log f_{\pm}) = -\frac{1}{\nu_1 + \nu_2} \int \frac{n_1}{n_2} \cdot d \log f_1.$$

These equations can be used in the ways which have already been described for the determination of the mean activities or activity coefficients.

Activity Coefficients in Dilute solutions of Single Salts and in Mixed Solutions. The variation of the activity coefficients of some typical salts with the concentration has been described in Part I, p. 168. In dilute solutions the activity coefficient decreases as the concentration is increased, but in most cases it reaches a minimum and increases again at higher concentrations. In very dilute solutions the activity coefficients of salts of the same ion type (e.g. uni-univalent) are very nearly the same. Lewis and Linhart * showed in 1919 that the activity coefficients in very dilute solutions could be represented by equations of the type $\log f_+ = -\beta c^{\alpha}$, and later Lewis and Randall and also Bronsted suggested that $\alpha' = 0.5$. This equation is only adequate in very dilute solutions. In stronger solutions another term, with a positive sign, becomes important. Harned † showed that the equation

$$\log f_{\pm} = -\beta c^{\alpha'} + \alpha c, \dots (162)$$

gave good agreement with the experimental values for many salts over a considerable range of concentration, when a' is close to 0.5.

In mixed solutions the following cases can be distinguished.

* J. Amer. Chem. Soc., 41, 1951, 1919. † Ibid., 42, 1808, 1920.

- (a) Mixtures of salts of the same ion type. The activity coefficient of any salt of the mixture depends on the total salt concentration, and in very dilute solutions is the same in all solutions of the same total normality. In stronger solutions the activity coefficient of a salt is influenced by the individual behaviour of all the various ions present.
- (b) Mixtures of salts of different ion types (e.g. HCl and K₂SO₄). In 1921 Lewis and Randall found that the effect of a bivalent ion on the activity coefficient of a salt was four times that of a univalent ion. In general, since the effect produced by an ion is proportional to the square of its valency, they introduced a quantity called the ionic strength.* This is obtained by multiplying the concentration of each ion by the square of its valency and dividing the sum of these products by two. Thus if m is the concentration of a given ion and z its valency, the ionic strength is

 $\mu = \sum mz^2/2$.

(The factor two is inserted so that for uni-univalent salts the ionic strength is equal to the total molar concentration.) Lewis and Randall stated the rule that in very dilute solutions the activity coefficient of a salt is the same in all solutions of the same ionic strength. It should be emphasized that this only holds in extremely dilute solutions ($\mu < 0.01$) and is to be regarded as the limiting law; in stronger solutions the activity coefficients are influenced by the individual characters of the various ions present.

The Debye-Hückel Calculation of the Activity Coefficient of a Strong Electrolyte. The possibility that strong

^{*} J. Amer. Chem. Soc., 43, 1112, 1921.

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electrolytes are completely dissociated, and that the behaviour which was ascribed in the Arrhenius theory to variations of the degree of dissociation was caused by the electric forces between the ions was suggested at various times by van Laar, Sutherland, Bjerrum and others. S. R. Milner * in 1912 made the first serious attempt to calculate the effect of the electric forces on the thermodynamic properties of salt solutions. Assuming that the electrolyte was completely dissociated into ions and that the distribution of the ions was determined by the electric forces between them, he attempted to calculate the electric potential energy of the solution by summing the potential energy of every pair of ions. Effectively this determines the electrical work which must be done in separating the ions to an infinite distance from each other, i.e. the electrical work done in an infinite dilution of the solution. This calculation is very complicated and its result will be referred to later.

In 1923 Debye and Hückel† devised a comparatively simple mathematical treatment of the problem, the essential parts of which are given below.

It is assumed that strong electrolytes are completely dissociated. This is an obvious necessity, for until the properties of a completely dissociated solution have been calculated it is impossible to tell whether there is any discrepancy which might be ascribed to incomplete dissociation. The calculation is concerned with two interrelated effects, (1) the average distribution of ions round a given ion, (2) the electrical potential near the surface of the given ion due to this distribution.

^{*} Phil. Mag., 23, 551, 1912; 25, 743, 1914; 35, 214, 352, 1918.

[†] *Physikal. Z.*, **24**, 185, 305, 1923. A simplified version is given by Debye, *ibid.*, **25**, 97, 1924.

Consider a solution containing n_1 ions of valency z_1 , n_2 ions of valency z_2 , n_3 ions of valency z_3 , etc., per c.c. Let ψ be the electric potential at a certain point in the vicinity of a given ion (i.e. the electric work which is done in bringing a unit charge to this point from an infinite distance). The work done in bringing an ion of charge $z_i\epsilon$ (where ϵ is the electronic charge) to the point in question is therefore $z_i\epsilon\psi$. If the concentration (per c.c.) of these ions at a great distance from the given ion $(\psi=0)$ is n_i , according to Boltzmann's equation the concentration at the point where the potential is ψ is $n_1e^{-z_i\epsilon\psi/kT}$, where k is the gas constant per molecule. The electric charge carried by these ions is thus

$$n_i(z_i\epsilon)e^{-z_i\epsilon\psi/kT}$$

per c.c. Summing this for all the ions present in the solution we therefore find that the total charge density (i.e. charge per c.c.) at a point where the electric potential is ψ is

 $\rho = \sum n_i(z_i \epsilon) e^{-z_i \epsilon \psi/kT}. \dots (163)$

Now an equation in electrostatics, viz. Poisson's equation, gives a relation between the variation of the electric potential at a point and the charge density. It is

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} = -\frac{4\pi\rho}{D}, \quad \dots (164)$$

where x, y, and z represent the rectangular co-ordinates of the point and D is the dielectric constant of the medium. The expression on the left of this equation is represented shortly by $\nabla^2 \psi$.

Substituting the value of ρ given by (163), we obtain

$$\nabla^2 \psi = -\frac{4\pi}{D} \sum n_i z_i \epsilon e^{-z_i \epsilon \psi / kT}. \dots (165)$$

An approximation to this equation can be made when $z_i \epsilon \psi$ is small compared with kT by substituting

$$1 - z_i \epsilon \psi / kT$$
 for $e^{-z_i \epsilon \psi / kT}$.

Then (165) becomes

$$abla^{\widehat{\jmath}\,,\cdot}
abla^{-}
abl$$

Since, when $\psi = 0$, there are as many positive as negative charges at any point, $\sum n_i z_i \epsilon$ is zero, and we are left with

$$\nabla^2 \psi = \kappa^2 \psi, \dots (166)$$

where

$$\kappa^2 = \frac{4\pi\epsilon^2}{DkT} \sum n_i z_i^2. \dots (167)$$

A solution of this equation giving ψ as a function of the distance r from the centre of the given ion can be written in the form

$$\psi = \frac{z\epsilon}{D} \cdot \frac{e^{-\kappa r}}{r} = \frac{z\epsilon}{Dr} - \frac{z\epsilon}{D} \cdot \frac{1 - e^{-\kappa r}}{r},$$

where $z\epsilon$ is the charge on the central ion. By electrostatic theory the first term $z\epsilon/Dr$ is the electric potential which is produced at the distance r by the charge $z\epsilon$ of the ion itself (it is assumed that the ion is spherical). The second term, which can be approximated to

$$\psi' = -\frac{z\epsilon\kappa}{D},$$

when κr is small compared with 1, is the potential at the given point produced by the surrounding distribution of ions (or ionic atmosphere). The potential at a point near the ion is thus

$$\psi = \frac{z\epsilon}{Dr} - \frac{z\epsilon\kappa}{D}, \dots (168)$$

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We may observe at this stage that ψ' is the potential at the surface of a sphere having the charge $-z\epsilon$ and the radius $1/\kappa$ in a medium of dielectric constant D. Accordingly $1/\kappa$ can be regarded as the equivalent radius of the ionic atmosphere (i.e. if the whole ionic atmosphere were concentrated at the radius $1/\kappa$ the potential produced would be the same). The value of $1/\kappa$ obtained by inserting the values of the universal constants in (167) for a uni-univalent electrolyte in aqueous solution is $1/\kappa = 3 \times 10^{-8}/\sqrt{c}$ cm., where c is the concentration in gram molecules per litre. For a 0.01N solution $1/\kappa$ is thus 30×10^{-8} cm., while the average distance between the ions in this case is 44×10^{-8} cm. It may also be observed that κ^2 is proportional to the ionic strength of the solution.

We now have to find the electric work done in transferring an ion from an infinitely dilute solution to a given solution. This can be regarded as the difference between the energy required to charge the ion in (1) an infinitely dilute solution, and (2) the given solution. In order to calculate these quantities it is supposed that it is possible to start with an uncharged ion and to build up the charge by infinitesimal amounts in such a way that at every stage the ion atmosphere adjusts itself so as to correspond with the amount of charge actually present.

If the potential at the surface of the ion (radius r_0) at any stage in this process is ψ , the work done in bringing up an element of charge de is ψde , and the total work done in giving the ion its charge $z\epsilon$ is given by the integral

$$w = \int_0^{ze} \psi \, de.$$

When the ion has the charge e the potential at its surface is by (168), $\psi = e/Dr_0 - e\kappa/D$,

In an infinitely dilute solution the second term disappears, since κ is then zero, and the work done in charging the ion is

$$w_0 = \int_0^{z\epsilon} \frac{e}{Dr_0} \cdot de = \frac{z^2 \epsilon^2}{2Dr_0}.$$

Similarly the work done in charging the ion in the given solution is

$$w = \! \int_0^{z\epsilon} \frac{e}{Dr_0} \cdot de - \! \int_0^{z\epsilon} \frac{e\kappa}{D} \cdot de = \! \frac{z^2\epsilon^2}{2Dr_0} - \frac{z^2\epsilon^2}{2D} \cdot \kappa.$$

The work done in transferring the ion from an infinitely dilute solution to the given solution is thus

$$W = w - w_0 = -z^2 \epsilon^2 \kappa / 2D. \quad \dots (169)$$

Now if there were no electric forces and the solutions were otherwise ideal, the free energy transfer of a single ion from a very dilute solution of concentration m_0 to a solution of concentration m would be

$$\Delta F_i = kT \cdot \log(m/m_0).*$$

Adding the work done on account of the electric forces (which is a free energy quantity since it was evaluated by a reversible process) we thus obtain, when there are no other effects which contribute to the free energy charge,

$$\Delta F_i = kT \cdot \log(m/m_0) + W.$$

But by definition,

or

$$\Delta F_i = kT \cdot \log(\alpha/\alpha_0) = kT \cdot \log(mf_i/m_0),$$

where f_i is the activity coefficient in the given solution, and the activity coefficient in the very dilute solution is 1. Comparing these equations it is evident that

$$kT \cdot \log f_i = W = -z_i^2 \epsilon^2 \kappa / 2D,$$

 $\log f_i = -z_i^2 \epsilon^2 \kappa / 2DkT.$ (170)

* k - R/N, where N° is the Avogadro number of the number of molecules in the gram molecule, is the gas constant per molecule.

In order to obtain the activity coefficient of a complete salt in a more practical form we may first observe that if n_i is the number of ions of species i per c.c., the number of gm. ions per litre is $c_i = n_i \cdot 1000/N_0$, where N_0 is the Avogadro number. Therefore

$$\sum n_i z_i^2 = \sum c_i z_i^2$$
. $N_0/1000$.

The value of κ^2 can thus be written as

$$\kappa^2 = \frac{4\pi\epsilon^2}{DkT} \cdot \frac{N_0}{1000} \; \Sigma c_i z_i^2, \label{eq:kappa}$$

and introducing this into (170), we have

$$\log f_i = -z_i^2 \left(\frac{\epsilon^2}{2DkT} \sqrt{\frac{4\pi\epsilon^2}{DkT} \cdot \frac{N_0}{1000}} \right) \sqrt{\Sigma \overline{c_i z_i^2}},$$

$$= -z_i^2 B \sqrt{\Sigma c_i z_i^2}, \qquad (171)$$

where B is the quantity within the brackets. The mean activity coefficient of a salt $A_{\nu_1}B_{\nu_2}$ is

$$\log f_{\pm} = (1/\nu_1 + \nu_2)(\nu_1 \log f_1 + \nu_2 \log f_2),$$

and therefore

$$\log_e f_{\pm} = -\sum \frac{v_1 z_1^2}{v_1 + v_2} \cdot B \sqrt{\Sigma c_i z_i^2}, \quad \dots (172)$$

where ν_1 is the number of ions of valency z_1 in the salt and the summation extends over all the ions.

The valency factor $\sum v_1 z_1^2 / (v_1 + v_2)$ has the values:

$$\begin{array}{ll} \text{for uni-univalent electrolytes, } \nu_1 = 1 \,, \, \nu_2 = 1 \,\,; \\ e.g. \,\, \text{KCl} \,\,; & z_1 = 1 \,, \, z_2 = 1 \,\,; \end{array} \} \,\, \sum \frac{\nu_1 z_1^{\,\,2}}{\nu_1 + \nu_2} = 1$$

$$\begin{array}{ll} \text{for uni-bivalent electrolytes,} \ \ \nu_1 = 1, \ \nu_2 = 2 \ ; \\ e.g. \ \ \text{CaCl}_2, \ \ \text{K}_2 \text{SO}_4 \ ; \\ \end{array} \ \ z_1 = 2, \ z_2 = 1 \ ; \\ \end{array} \right\} \ \sum \frac{\nu_1 z_1^2}{\nu_1 + \nu_2} = 2$$

$$\begin{array}{ccc} \text{for uni-trivalent electrolytes,} & \nu_1 = 1, \; \nu_2 = 3 \; ; \\ e.g. \; \; \text{LaCl}_3, \; \text{K}_3 \text{Fe}(\text{CN})_6 & z_1 = 3, \; z_2 = 1 \; ; \\ \end{array} \sum \frac{\nu_1 z_1^2}{\nu_1 + \nu_2} = 3$$

$$\begin{array}{ll} \text{for bi-bivalent electrolytes,} & \nu_1 = 1 \,, \; \nu_2 = 1 \,; \\ e.g. \; \text{CaSO}_4 \;; & z_1 = 2 \,, \; z_2 = 2 \,; \\ \end{array} \\ \begin{array}{ll} \sum \frac{\nu_1 z_1^2}{\nu_1 + \nu_2} = 4 \\ \text{for bi-trivalent electrolytes,} & \nu_1 = 2 \,, \; \nu_2 = 3 \,; \\ e.g. \; \text{Fe}_2(\text{SO}_4)_3 \;; & z_1 = 3 \,, \; z_2 = 2 \,; \\ \end{array} \\ \begin{array}{ll} \sum \frac{\nu_1 z_1^2}{\nu_1 + \nu_2} = 6 \\ \end{array}$$

Tests of the Debye-Hückel Equation. In very dilute solutions it is often convenient to use the weight concentration (m) instead of c. If d is the density of the solvent, we can write for dilute solutions, without appreciable error, $c_i = m_i/d$; or $\sum c_i z_i^2 = \sum m_i z_i^2/d$, and since

where $B' = B/\sqrt{a}$. Using the constants,

$$\epsilon = 4.77 \times 10^{-10} \text{ e.s.u.}, N^{\circ} = 6.06 \times 10^{23},$$

 $k=1\cdot371\times10^{-16}$ ergs, the value of $\sqrt{2B'}/2\cdot303$ for water is found to be $0\cdot489$ at $0^{\circ},\,0\cdot504$ at $25^{\circ},\,0\cdot526$ at $50^{\circ}.$ We can take its value as $0\cdot50$ at $25^{\circ},$ with sufficient accuracy. The following equations are then obtained for the activity coefficients of electrolytes of various types at $25^{\circ}.$

 $\begin{array}{ll} \text{Uni-univalent}: & \log_{10} f_{\pm} = -0.5 \sqrt{\mu}. \\ \text{Uni-bivalent}: & \log_{10} f_{\pm} = -1.0 \sqrt{\mu}. \\ \text{Uni-trivalent}: & \log_{10} f_{\pm} = -1.5 \sqrt{\mu}. \\ \text{Bi-bivalent}: & \log_{10} f_{\pm} = -2.0 \sqrt{\mu}. \\ \text{Bi-trivalent}: & \log_{10} f_{\pm} = -3.0 \sqrt{\mu}. \end{array}$

On account of the approximations which have been made in the derivation and of certain factors which will be considered later, these equations can only be expected to apply at very small concentrations (μ <0.01).

Brönsted and La Mer * have made a test of these equations by determining the activity coefficients of some complex cobaltammine salts of various ion types in salt solutions, by the solubility method. Their curves, which are shown in Fig. 12, are in excellent agreement

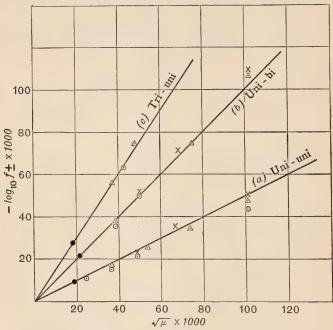


Fig. 12.—Activity coefficients of salts of various types in mixtures (Brönsted and La Mer):

- (a) $[\mathrm{Co(NH_3)_4NO_2}$, $\mathrm{CNS}]^+[\mathrm{Co(NH_3)_2(NO_2)_2C_2O_4}]^-.$ Uni-univalent.
- (b) $\left[\operatorname{Co(NH_3)_4C_2O_4}\right]_2^+ \left[\operatorname{S_2O_6}\right]^=$. Uni-bivalent.
- $\begin{array}{c} \text{(c) } \{\operatorname{Co}(\operatorname{NH_3})_6\}^{+++} \Big[\operatorname{Co}(\operatorname{NH_3})_2(\operatorname{NO}_2)_2\operatorname{C}_2\operatorname{O}_4\Big]_3^- \text{.} & \operatorname{Tri-univalent.} \\ \operatorname{Added salt}; & -\bigcirc -\operatorname{NaCl}, & -\triangle -\operatorname{KNO}_3, & -\times -\operatorname{K}_3\operatorname{Co}(\operatorname{CN})_6, \\ & \mathbb{E} -\operatorname{BaCl}_2, & -\bullet \text{none.} \end{array}$

* J. Amer. Chem. Soc., 46, 555, 1924.

with the requirements of the theory. Nonhebel * determined the activity coefficients of hydrochloric acid at very small concentrations in aqueous solutions and found that the results were best represented by the equation $\log f = -0.39\sqrt{c}$, which is considerably different from the result of the Debye calculation, but quite close to that of Milner. Carmody obtained appreciably different results,† working in silica vessels, but Wynne-Jones has shown ‡ that if a correction is made in Nonhebel's data for the solution of alkaline impurities from the glass used, good agreement between the two sets of values is obtained, and the slope of the activity coefficient curve at very small concentrations is then in excellent agreement with Debye and Hückel's calculation.

Numerous other tests have been made of the theoretical equation. According to (171) B should be proportional to $1/(DT)^{3/2}$. This has been tested by measurements in aqueous solutions at temperatures other than 25°. For example, Baxter determined the activity coefficients of silver iodate in salt solutions at 75° and found agreement with the theory.§ The dielectric constant of the medium can also be varied by adding neutral substances, such as sugar, alcohol, etc. It is necessary to interpret the results in such solutions with caution for, as will be shown later, substances having a dielectric constant less than water are "salted out" from the vicinity of the ions. The addition of alcohol to a salt solution will thus affect the dielectric constant of the medium only at an appreciable distance from the ions. It has, however, been

^{*} Phil. Mag., 2, 586, 1926.

[†] J. Amer. Chem. Soc., 54, 188, 1932.

[‡] Ibid., **54**, 2130, 1932.

[§] J. Amer. Chem. Soc., 48, 615, 1926.

shown by Pauling* that variations of the dielectric constant of the medium very near the ions have very little effect on the limiting equation. Numerous measurements of the value of B in the presence of non-electrolytes have been made, e.g. with hydrogen chloride in aqueous glycerol solutions by Lucasse,† and in sucrose solutions by Scatchard,‡ in which reasonable agreement with the theory has been obtained. Butler and Robertson \S determined the activity coefficients of hydrogen chloride in water-ethyl alcohol solvents extending from pure water to pure alcohol, and found that B varied approximately linearly with $1/(DT)^{3/2}$ over the whole range of solvents. A similar result was obtained by Åkerlöf $\|$ with hydrochloric and sulphuric acids in water-methyl alcohol solutions.

*Activity Coefficient of the Solvent and the Total Electrical Energy of the Solution. The partial free energy of the solvent can be determined by the use of $d\bar{F}_1 = -n_2/n_1$. $d\bar{F}_2$, where n_2 and n_1 are the number of mols of solute and solvent. If m is the number of mols of the solute to 1000 gms. solvent then $n_2/n_1 = m_2 M_1/1000$ ($M_1 = \text{mol.}$ wt. of solvent). The value of \bar{F}_2 for a uni-univalent salt in dilute solutions, introducing the Debye-Hückel correction for the electrical forces and remembering that there are two ions in a molecule of salt, is

$$\overline{F}_2\!=\!\overline{F}^{\,\circ}_{\,\,2}+2RT$$
 , $\log\,m_2-2RT$, $B'\sqrt{2m_2}.\P$

^{*} J. Amer. Chem. Soc., 47, 2129, 1925.

[†] Ibid., 48, 626, 1926.

[†] Ibid., 48, 2026, 1926.

[§] Proc. Roy. Soc., A, 125, 694, 1929.

^{||} J. Amer. Chem. Soc., 52, 2353, 1930.

 $[\]P[\overline{F}_2 = \overline{F}_2^{\circ} + 2RT \log m_2 + 2RT \log f_{\pm}, \text{ and } \log f_{\pm} = -B'\sqrt{2m_*}]$

Therefore,

$$d\bar{F}_2/dm_2 = 2RT/m_2 - 2RT$$
 . $B'(\sqrt{2}/2)m_2^{-\frac{1}{2}}$

and

$$d{ar F}_1/dm_2$$

$$=-(m_2M_1/1000)[2RT/m_2-2RT\cdot B'(\sqrt{2}/2)m_2^{-\frac{1}{2}}].$$

Integrating this, we obtain

$$\bar{F}_1 = \bar{F}^{\circ}_1 - 2RT(m_2M_1/1000) \left[1 - \frac{B'\sqrt{2m}}{3}\right]...(174)$$

Comparing with (129a), it can be seen that the ideal equation for the lowering of the partial free energy of the solvent by 2 gm.-ions of salt is

$$\bar{F}_1 = \bar{F}^{\circ}_1 - 2RT(n_2/n_1).$$

We can write (174) as

$$\bar{F}_1 = \bar{F}^{\circ}_1 - 2RT(n_2/n_1)(1-\phi),$$

where the correction factor ϕ has been called the "osmotic coefficient."* According to the Debye-Hückel calculation it is thus evident that $\phi = (B'\sqrt{2m})/3$.

If the solution contains n_1 mols of the solvent to n_2 mols of the solute, the quantity of solvent to 1 mol of solute is n_1/n_2 . By (117) the total free energy of that quantity of solution which contains 1 mol of the salt is

$$F = \overline{F}_2 + (n_1/n_2) \overline{F}_1.$$

We can obtain the total electrical free energy of the solution by introducing into this equation the electrical

* Bjerrum, Z.f. Electrochem., 24, 321, 1918. Brönsted, J. Amer. Chem. Soc., 42, 761, 1920; 44, 877, 938, 1922.

contributions to \bar{F}_1 and \bar{F}_2 , which have now been determined. The electrical contribution to \bar{F}_2 is

$$-2RT \cdot B'\sqrt{2m}$$
,

and to \bar{F}_1 is

$$+2RT.(n_2/n_1)(B'\sqrt{2m}/3).$$

That part of the total free energy of the solution which is due to the electrostatic forces between the ions (for 1 mol of salt) is

$$F_e = -2RT \cdot B'\sqrt{2m} + (2RT \cdot B'\sqrt{2m})/3$$

= $-(2/3)2RT \cdot B'\sqrt{2m}$,(175)

or, in terms of the volume concentration,

$$F_e = -(2/3)2RT \cdot B\sqrt{2c} \cdot \dots (175a)$$

The total electric free energy, which is the work done on account of the electric forces in diluting the solution with an infinite quantity of the solvent, *i.e.* the electric work of separating the ions of a mol of salt to an infinite distance from each other, is thus equal to two-thirds of the partial molar free energy of the salt.

Milner evaluated this quantity directly and obtained the result in the form

$$F_e = -RT \cdot h \cdot f(h),$$

where $h = \frac{1}{10} \left(\frac{8\pi N^{\circ} c}{3} \right)^{1/3} \frac{\epsilon^2}{DkT}$, and f(h) is a complicated

function whose values have not been determined with any great accuracy. If $hf(h) = (2/3)\sqrt{3}h^3$, this expression becomes equal to that derived from the Debye-Hückel equation, since

$$\sqrt{3h^3} = 2\sqrt{\frac{\pi N^{\circ}}{1000}} \cdot \frac{\epsilon^3}{(DkT)^{3/2}} \sqrt{2c} = 2B\sqrt{2c}.$$

Some ratios of hf(h) to $\sqrt{3h^3}$ are given in the following table,* and it can be seen that although the divergence is comparatively small, the values are somewhat greater than 2/3 in dilute solutions.

 $-hf(h)/\sqrt{3h^2}$. -hf(h). C. h. 0.00010.05590.01680.7340.001 0.1200.05250.7280.002 0.1520.07350.7150.0050.2060.1140.7040.010.2590.1590.6960.02 0.3270.2220.6850.050.4430.3450.6750.100.5590.4860.6700.200.6720.656 0.704

TABLE XII.

The result of the Milner calculation is thus of the same form as that of Debye, but gives a slightly different and variable value of B.

Extension to Concentrated Solutions. In estimating the potential at the surface of an ion due to the ionic atmosphere, the following approximation has been made:

$$\psi' = \frac{z\epsilon}{D} \cdot \frac{1 - e^{-\kappa r}}{r} \to \frac{z\epsilon}{D} \kappa.$$

When κr is not very small this needs amendment. A closer approximation is given by the equation

$$\psi' = \frac{z\epsilon}{D} \cdot \frac{\kappa}{1 + \kappa r},$$

If r_i is the radius of the ion, the potential at its surface * Noyes, J. Amer. Chem. Soc., 46, 1080, 1924.

is obtained by substituting r_i in this expression, and we then obtain

$$\log f_i = -\frac{z_i^2 \epsilon^2}{2DkT} \cdot \frac{\kappa}{1 + \kappa r_i}$$

$$= -\frac{z_i^2 B \sqrt{c_i z_i^2}}{1 + A r_i \sqrt{c_i z_i^2}}, \dots (176)$$

$$A = \sqrt{\frac{4\pi \epsilon^2}{D\kappa T}} \cdot \frac{N^{\circ}}{1000}.$$

where

For aqueous solutions $A = 0.232 \times 10^8$. This expression will apply to a uni-univalent salt if it be assumed that the ionic radius is the same for both ions, or that r_i is the mean ionic radius. Using reasonable values for the ionic radii, this expression fits the experimental data to a higher concentration than the original equation. That it fails in more concentrated solutions is obvious from the fact that in many cases the activity coefficient passes through a minimum and increases, becoming greater than unity in strong solutions, i.e. $\log f$ becomes positive and (176) is incapable of giving positive values. shows the calculated and observed values of $\log f_+$ for NaCl. Log f' is the original equation (171) which represents the limiting slope at small concentrations; $\log f''$ represents equation (176), using $r = 2.35 \times 10^{-8}$ cm., while the dashed line represents the observed behaviour. It is evident that in strong solutions we need a positive term, which, according to the empirical equation (162), should be linear with the concentration.*

^{*} A close examination of the approximations made in the Debye-Hückel theory and the effect of the ionic radii has been made by Gronwall, La Mer and Sandved (*Physikal. Z.*, 29, 558, 1928; *J. Physical Chem.*, 35, 2245, 1931).

Hückel's theory of concentrated solutions. So far, the problem has been regarded as the calculation of the mutual electrical energy of charged particles in a medium of uniform dielectric constant. The medium only enters

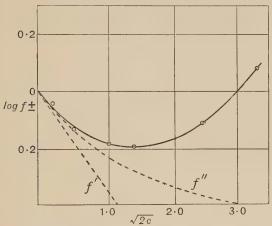


Fig. 13.—Calculated and observed activity coefficients of sodium chloride.

into the calculation in so far as it provides the dielectric constant D. In water and similar solvents, the molecules of the solvents carry electric dipoles and are themselves attracted by the ions. The electric forces in the immediate vicinity of ions are extremely powerful, e.g. it can be calculated, taking the dielectric constant of water as 80, that at 3×10^{-8} cm. from the centre of a univalent ion the electric field is 2×10^6 volts/cm. This intense field has two consequences. In the first place, the attraction of fields of this strength on the molecules of the solvent may be of the same order as that on oppositely charged ions. Consequently there will be a

tendency for ions to be "crowded out" from the immediate vicinity of an ion, i.e. there will be superimposed on the "coulomb forces," which have already been considered, an effective repulsive force which must be taken into account in order to obtain the distribution of ions round a given ion. Secondly, it has been assumed that the dielectric constant has a uniform value throughout the solution. The dielectric constant is a measure of the polarisation produced in a medium by an applied electric field, and is due partly to the orientation in the direction of the field of the permanent dipoles which may be present in the molecules, and partly to the electric charges within the molecule under the influence of the applied field. In the intense fields of force near the ions the permanent dipoles become completely orientated and the induced polarisation is so great that the effect of any increase in the applied field is no longer proportional to its amount. Under these circumstances the solvent near the ions becomes "electrically saturated," and its dielectric constant may be considerably less than the normal value.* The dielectric constant of the medium in a salt solution will thus vary from point to point, and the average value for the whole of the solvent will be less than that of the pure solvent.

A precise calculation of the effect of these phenomena on the activity coefficients of ions is extremely difficult. Hückel† assumed that both effects might be introduced into the equations by regarding the average dielectric constant of the medium as a function of the salt concentration. The lowering of the dielectric constant by the

^{*} Herweg (Z. f. Physik, 3, 36, 1922) demonstrated that the dielectric constant of water dininishes in intense electric fields.

[†] Physikal. Z., 26, 93, 1925.

factors mentioned above should be proportional to the number of ions, and we may write

$$\begin{split} D = D_0 - \delta_1 c_1 - \delta_2 c_2, \text{ etc.,} \\ = D_0 - \bar{\delta} c, \end{split}$$

where c_1 , c_2 , etc., are the concentrations of ions of different kinds (mols per litre of solution), and δ_1 , δ_2 , etc., the coefficients of the dielectric constant lowering produced by them.

This variation of the dielectric constant affects the work of charging the ion on account of the potential due to its own charge, as well as the work done on account of the potential of the ionic atmosphere. The work of charging the ion in an infinitely dilute solution is $w_0 = z^2 \epsilon^2 / 2 D_0 r_i$, and the work of charging the ion in the given solution, apart from the terms arising from the ionic atmosphere, is $w_0' = z^2 \epsilon^2 / 2 D r_i$. The quantity

$$w'=z^2\epsilon^2/2Dr_i-z^2\epsilon^2/2D_0\,r_i$$

must thus be added to the term arising from the potential of the ionic atmosphere, viz. $\psi' = \frac{z\epsilon}{D} \cdot \frac{\kappa}{1 + \kappa r_i}$. In evaluating $\int_0^{z\epsilon} \psi' de$ it is also necessary to regard D as a function of the concentration. Hückel obtained the result of this calculation in the form

$$\log f_i = \frac{{z_i}^2 \epsilon^2}{2D_0 kT} \; \frac{\kappa_0}{1+\kappa_0 \; r_i} + f(\kappa), \label{eq:fitting}$$

where κ_0 is the value of κ corresponding to D_0 , and $f(\kappa)$ is a complicated function which was found to be nearly proportional to the ionic concentration. For a uniunivalent salt we thus obtain

$$\log f_{\pm} = -\frac{B\sqrt{2c}}{1 + A\bar{r}\sqrt{2c}} + C \cdot 2c, \quad \dots (177)$$

i.e. as the result of assuming a lowering of the dielectric constant of the medium which is proportional to the concentration of the salt, we obtain an additional positive term for $\log f_{\pm}$ which is proportional to the concentration.

In very dilute solutions the *ideal* equation for the partial free energy of a salt may be written equally well in terms of the molar ratio of the salt to solvent molecules (or the related quantity m) or the molar fraction of the salt, for n_2/n_1 does not differ appreciably from n_2/n_1+n_2 when n_2 is small. But in concentrated solutions these quantities may differ appreciably. Hückel thought that the ideal equation for the partial free energy of a salt was properly expressed in terms of the molar fraction of the ions, *i.e.* for a binary electrolyte

$$\overline{F}_2 {=} \overline{F}^{\circ}_2 + 2RT \log \frac{\Sigma n_2}{\Sigma n_2 + n_1},$$

where Σn_2 is the total number of ions and n_1 the number of solvent molecules. If we use an expression of the kind

$$\overline{F}_2 = \overline{F}^\circ_2 + 2RT \cdot \log{(\Sigma n_2/n_1)}$$

it is therefore necessary to make a correction which is equal to the difference between these expressions. This correcting term is $2RT \log (n_1/(n_1+\Sigma n_2))$. If the solution contains m gram molecules of salt to 1000 grams of the solvent, of molecular weight M_1 , we have

$$\frac{n_1}{n_1 + \Sigma n_2} \!\! = \!\! \frac{1000/M_1}{(1000/M_1) + 2m} \!\! = \! 1 \! \left/ \! \left(1 + \!\! \frac{2mM_1}{1000} \right) \! \cdot \right.$$

Inserting this correction into the activity coefficient (177) we thus have

$$\log f_{\pm} = -\frac{B\sqrt{2c}}{1 + A\overline{r}\sqrt{2c}} + C \cdot 2c - \log\left(1 + \frac{2mM_1}{1000}\right). \quad (178)$$

This equation is similar in form to Harned's empirical equation, and by a suitable choice of the constants a and

C can be made to fit the experimental data over a considerable range of concentration. There are two adjustable constants \bar{r} and C (A and B are absolute constants which can be calculated), \bar{r} being the mean ionic radius for the salt and C a function of the dielectric constant lowering coefficient $\bar{\delta}$. Fig. 14 shows curves of $\log f$ calculated by Hückel for various values of $\bar{\delta}$.

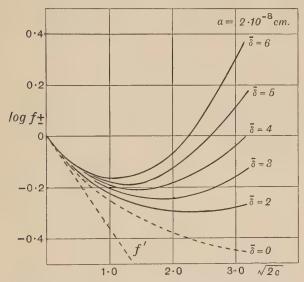


Fig. 14.—Theoretical curves of activity coefficients for various values of δ (Hückel).

The values of the Debye-Hückel constants for a number of salts, as determined by Harned and Åkerlöf,* are given in Table XIII.

^{*} Physikal. Z., 27, 411, 1926.

TABLE XIII.

Salt.		$\bar{r} \times 10^8$.	C.	δ.
KCl -	-	3.38	0.017	3.2
NaCl -	-	3.62	0.028	5.5
LiCl -	-	3.62	0.0698	11.5
HCl -	-	3.38	0.0805	11.8
KOH -	-	3.35	0.0632	9.65
NaOH	-	2.87	0.050	6.45
LiOH -	-	$2 \cdot 15$	0.0215	2.2
BaCl ₂ -	-	3.83	0.0285	7.14
SrCla -	-	4.39	0.030	8.93
CaCl ₂ -	- 1	4.35	0.060	14.61

Although Hückel's theory succeeds in deriving a linear term in the expression for $\log f_{\pm}$, it is not known whether the values of δ which are required to give agreement with the experimental data actually correspond with the effect of the salt on the dielectric constant of the solvent.* It is doubtful if the large values of δ required in certain cases can have a real physical meaning. It might also have been expected that the values of δ would be additive for the different ions, but it can be seen that whereas in the chlorides the values of δ are in the order Li>Na>K, in the case of the hydroxides the reverse order, K>Na>Li, is obtained (see Part I, Fig. 39, p. 169).

Solvation of Ions. Many lines of evidence indicate that ions are solvated in solution, *i.e.* they carry with them a sheath of the solvent, which is firmly attached either by the attraction of the electric field of the ions on the dipoles of the solvent molecules or possibly by some kind of electronic interaction. A linear term in the equation for $\log f_{\pm}$ can be derived in a very simple way

^{*} Walden, Ulich and Werner, Z. phys. Chem., 116, 261, 1926.

as a result of this solvation.* The solvent molecules which are attached to the ions are effectively withdrawn from the solution and the real concentration of the ions is thereby increased. For the purpose of computing this effect the concentration of an ion is best expressed as its molar ratio. If the solution contains n_1 molecules of the solvent and n_i ions of the *i*th kind, the apparent molar ratio of the ions to the solvent is n_i/n_1 , and in the absence of solvation the partial free energy of these ions, neglecting the effect of the interionic forces, would be represented by

$$\bar{F}_i = \bar{F}_i^{\circ} + RT \log n_i/n_1$$
.

But if each ion is, on the average, solvated by h solvent molecules the effective number of the latter in the solution is $n_1 - \sum n_i h$, where the summation extends over all the ions present. (178) must therefore be replaced by

$$\begin{split} \overline{F}_i &= \overline{F}^{\circ}{}_i + RT \cdot \log \frac{n_i}{n_1 - \Sigma n_i \overline{h}} \\ &= \overline{F}^{\circ}{}_i + RT \log \frac{n_i}{n_1 (1 - (\Sigma n_i \overline{h}/n_1))} \\ &= F^{\circ}{}_i + RT \cdot \log n_i / n_1 - RT \cdot \log (1 - (\Sigma n_i \overline{h})/n_1). \end{split}$$

The additional factor may be written as $RT \log f_i *$, where $f_i *$ is that part of the activity coefficient which arises from solvation. To a first approximation we may write

$$\log f_i * = -\log(1 - (\sum n_i h) n_1) = (\sum n_i h) / n_1. \dots (179)$$

If m_i is the molar (weight) concentration per 1000

^{*} Cf. Bjerrum, Z. anorg. Chemie, 109, 278, 1920.

grams of solvent, we have $n_i/n_1 = m_i M_1/1000$, where M_1 is the molecular weight of the solvent. Then (179) becomes

$$\log_e f_i * = \sum m_i h M_1 / 1000.$$

 f_i * is the same for all the ions present in the solution, so that the mean value of f_i * for the salt is also given by

$$\log_{10} f_{\pm} * = \sum m_i h M_1 / 2 \cdot 3 \times 1000.$$
(180)

We can equate this with the final term of (177), which may be written for this purpose in the form:

$$\log f_{\pm} * = C \cdot \sum m_i z_i^2$$
,

and we then obtain

$$C = \frac{\sum m_i}{\sum m_i z_i^2} \cdot \frac{M_1 \cdot h}{2 \cdot 3 \times 1000} \cdot \dots (181)$$

The following table gives the values of h (the average effective hydration per ion) which would be required to account for the observed values of C in aqueous solutions.

TABLE XIV.

KCl	$2 \cdot 2$	KOH	8.1	$BaCl_2$	$7 \cdot 3$
NaCl	$3 \cdot 6$	NaOH	$6 \cdot 4$	$SrCl_2$	7.7
LiCl	8.9	LiOH	$2 \cdot 7$	$CaCl_2$	15.3
HCl	10.3			-	

While in most cases these are fairly reasonable magnitudes, the difficulty again arises that the values are not additive for the different ions as we should expect hydration values to be. A complete solution of the problem thus awaits a more complete mathematical

treatment of the forces between the ions and the solvent.*

Activity Coefficients in Mixtures of Strong Electrolytes. While in very dilute solutions of a mixture of salts the activity coefficient of a salt is determined, at least approximately, by the ionic strength rule, in concentrated solutions it depends on the nature of the other ions present. In order to determine the activity coefficient of a salt in such a solution it is generally necessary to resort to electromotive methods. For example, the partial free energy of hydrogen chloride in the presence of other chlorides can be determined from the electromotive forces of cells of the type

$$H_2 \mid HCl(m_1), MCl(m_2), AgCl(s) \mid Ag.$$

The activity coefficient of HCl in this cell can be determined by comparison with the cell:

$$H_2 \mid HCl(m), AgCl(s) \mid Ag,$$

for which the activity coefficient of HCl is known. Extensive measurements of cells of this type have been made by Harned and his co-workers,† and by others. Their main conclusions are summarised below.

- (1) Salt mixtures of constant total concentration. When the total electrolyte concentration $(m_1 + m_2)$ remains
- * Butler (J. Phys. Chem., 33, 1015, 1929) has attempted to account for the linear term in the expression for log f as a consequence of the "salting out" of the ions by each other (see p. 164). Dielectric constant lowering, solvation, mutual "salting out" are only different ways of regarding the same phenomenon. This calculation does, however, demand somewhat smaller dielectric constant lowerings than Hückel's.
- † Summaries by Harned and Åkerlöf, *Physikal. Z.*, 27, 411, 1926; Harned, *Trans. Far. Soc.*, 23, 462, 1927.

constant it is found that $\log f_1$ varies linearly with m_1 . Fig. 15 shows the values of $\log f_1$ in lithium, sodium and potassium chloride solutions of total concentration $(m_1 + m_2) = 3$. Similar results have also been obtained in more dilute solutions, e.g. Güntelberg obtained a

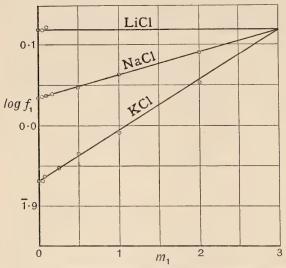


Fig. 15.—Activity coefficients of HCl in alkali chloride solutions at constant total concentration $(m_1+m_2=3)$. (Harned and Åkerlöf.)

similar relation for a total concentration $\Sigma m = 0.1.*$ The curves shown in Fig. 16 are obtained when f_1 is plotted against log m_1 . It can be seen that when the concentration of hydrogen chloride is very small its activity coefficient is practically independent of m_1 and depends only on the nature and concentration of the solution in which it is dissolved.

^{*} Z. physikal. Chem., 123, 199, 1926.

(2) Acid concentration constant, salt concentration variable. When m_1 is kept constant and m_2 varied, the

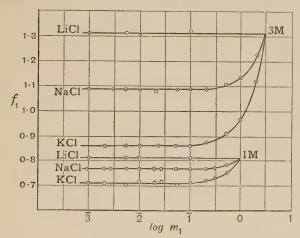


Fig. 16.—Activity coefficients of HCl in alkali chloride solutions at constant total concentrations $m_1+m_2=1$ and $m_1+m_2=3$. (Harned and Åkerlöf.)

curves obtained are very similar to the curves for the single salts. Fig. 17 shows the activity coefficients of hydrogen chloride at $m_1 = 0.01$ and 0.1 in solutions of lithium, sodium and potassium chlorides.

This behaviour is in good agreement with the requirements of the Debye-Hückel theory. Writing the equation for the mean activity coefficient of a salt in the semi-empirical form

$$\log f_{\pm} = -\beta \sqrt{\sum m_i z_i^2 + \sum \lambda m_i},$$

it can be seen that the first term which represents the effect of the interionic forces will be constant in solutions of constant total ionic strength and the variation of $\log f_{\pm}$ will depend on the linear term $\Sigma \lambda m_i$. According to Hückel's theory we should expect that each kind of ion has its specific constant, and that the value of this term

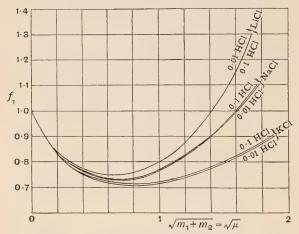


Fig. 17.—Activity coefficients of hydrogen chloride in alkali chloride solutions.

 $m_1 = \text{const.}, m_2 = \text{variable.}$ (Harned and Åkerlöf.)

for a mixed solution is made up of the sum of the terms for the various ions present. Thus, in solutions of $HCl(m_1)$ and $KCl(m_2)$, we have

(a)
$$m_1 + m_2 = \text{constant } (m)$$
.

$$\log f_1 = -\beta \sqrt{\sum m_i z_i^2} + \lambda_1 m_1 + \lambda_2 m_2$$

$$= (\lambda_1 - \lambda_2) m_1 + \lambda_2 m + \text{constant } ;$$

i.e. $\log f_1$ varies linearly with m_1 .

(b)
$$m_1$$
 constant; m_2 variable.

$$\log f_1 = -\beta \sqrt{\sum m_i z_i^2} + \lambda_1 m_1 + \lambda_2 m_2.$$

When m_1 is small, the variation of $\log f_1$ will be determined mainly by the interionic term $-\beta\sqrt{\sum m_i z_i^2}$ and by $\lambda_2 m_2$. The curve for f_1 will thus be very similar to the curve for $\log f_2$ in a pure solution of the salt. In pure solutions of a series of salts of the same ion type, $\log f_2$ will be greater at a given concentration the greater the value of λ_2 . It therefore follows that the activity coefficient of HCl, when present at a small constant concentration in a series of salt solutions of the same strength, should be greatest in that solution for which $\log f_2$ has the greatest value. Thus, since for a given concentration the activity coefficients of the alkali metal chlorides are in the order

$$f_{
m LiCl} > f_{
m NaCl} > f_{
m KCl}$$

we should find for the activity coefficients of HCl in the same solutions

$$f_{\mathrm{HCl\,(LiCl)}} > f_{\mathrm{HCl\,(NaCl)}} > f_{\mathrm{HCl\,(KCl)}}.$$

Fig. 17 shows that this is the case. The same is also true for hydrogen chloride in solutions of the alkaline earth chlorides, and for sulphuric acid in the alkali sulphates.

Anomalous behaviour of hydroxides. The reverse, however, is the case for the strong hydroxides. It has been observed already that these electrolytes are anomalous in pure aqueous solution. At a given concentration in pure water their activity coefficients are in the order

$$f_{\text{KOH}} > f_{\text{NaOH}} > f_{\text{LiOH}}$$
.

Similarly, in mixed solutions containing salts of a given ion type, it is found that, at a given hydroxide and total concentration, the activity coefficients of the strong hydroxides are less in the solution of the salt which has

the higher activity coefficient itself. Thus, Harned and his co-workers found that

 $f_{ ext{KOH (KCl)}} > f_{ ext{NaOH (NaCl)}} > f_{ ext{LioH (Licl)}},$

and $f_{\text{KOH}(\text{KCl})} > f_{\text{KOH}(\text{KBr})} > f_{\text{KOH}(\text{KI})};$

while $f_{\text{LiCl}} > f_{\text{NaCl}} > f_{\text{KCl}}$,

and $f_{\text{KI}} > f_{\text{KBr}} > f_{\text{KCl}}$.

This is the reverse of what would be expected by Hückel's theory, or on any theory in which the linear term is additive for the various ions. Harned has suggested as a possible cause of this behaviour the highly unsymmetrical nature of the hydroxide ion, which will therefore be easily deformed by an electric field. The extent of this deformation will be greater the greater the field intensity, and in the presence of lithium ions the hydroxide ion will thus be less symmetrical than in the presence of sodium ions.

The Apparent Molar Volumes of Salts. It has been found that the apparent molar volumes of salts in aqueous solution increase linearly with the square root of the concentration,* i.e. $\phi = \phi_0 + a\sqrt{c}$, where ϕ_0 is the apparent molar volume at infinite dilution, a a constant and c the concentration (mols per litre). In Fig. 18, which shows the data for a number of salts, it can be seen that this relation holds over a considerable range of concentration. This is true of many salts in aqueous solution.

A similar relation can easily be derived for the partial molar volumes. In dilute aqueous solutions the weight concentration m_2 does not differ very greatly from c, and

^{*} Masson, Phil. Mag., 8, 218, 1929; Geffcken, Z. physikal. Chem., A, 155, 1, 1931; Scott, J. Physical Chem., 35, 2315, 1931.

we may write $\phi = \phi_0 + a\sqrt{m_2}$. Substituting this value of ϕ in (99), viz. $d\phi/d \log m_2 + \phi = \overline{V}_2$, where \overline{V}_2 is the partial molar volume of the salt, we obtain

$$\bar{V}_2 = \phi_0 + 3a/2\sqrt{m_2}$$
....(182)

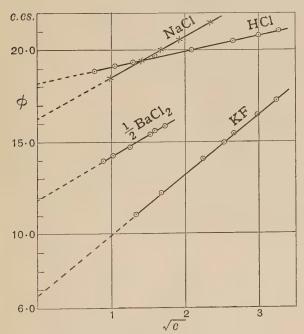


Fig. 18.—Apparent molar volumes of salts in aqueous solution at 25°.

A derivation of the value of a in dilute solutions from the Debye-Hückel equation for the free energy of strong electrolytes has been given by Redlich and Rosenfeld.* By (142) the variation of the partial free energy of a

^{*} Z. physikal. Chem., A, 155, 65, 1931.

component with the pressure is equal to its partial molar volume. Introducing the value of the activity coefficient given by Debye and Hückel's equation for very dilute solutions, we may write for the partial free energy of a uni-univalent electrolyte

$$\begin{split} \bar{F}_2 - \bar{F}^{\circ}_{2} = & 2RT \log m - 2RT \cdot B\sqrt{2c}, \\ B = & \frac{\epsilon^3}{(DkT)^{3/2}} \sqrt{\frac{\pi N_0}{1000}}. \end{split}$$

where

Differentiating this with respect to the pressure, we have

$$\left[\frac{d(\bar{F}_2 - \bar{F}^{\circ}_2)}{dP}\right]_{T, m} = RT \cdot B\left(\frac{3}{D} \cdot \frac{\partial D}{\partial P} - \beta\right) \sqrt{2c},$$

where $\partial D/\partial P$ is the variation of the dielectric constant of the solvent with the pressure, and $\beta = (1/V)\partial V/\partial P$ is the compressibility of the solvent. By (142) we can also write

$$\left[\frac{d(\bar{F}_2 - \bar{F}^{\circ}_2)}{dP}\right]_{T, m} = \bar{V}_2 - \bar{V}^{\circ}_2,$$

where \overline{V}_2 , \overline{V}°_2 are the partial molar volumes of the salt in the given solution and at infinite dilution. Comparing with (182), it is evident that

$$a = \frac{2RT\sqrt{2}B}{3} \left(\frac{3}{D} \cdot \frac{\partial D}{\partial P} - \beta\right). \dots (183)$$

Using the available measurements of the variation of the dielectric constant of water with the pressure, and its compressibility, Redlich and Rosenfeld calculated $a=1.8\pm0.6$. Considering the uncertainty of $\partial D/\partial P$, this is in reasonable agreement with the observed values, a few of which are given in Table XV.

TABLE XV.

Apparent Molar Volumes of Salts in Water and Methyl Alcohol.

$$(\phi = \phi_0 + a\sqrt{c}).$$

	LiCl.	NaCI.	KCl.	NaI.	KI.	RbCl.
In H_2O^* ϕ_0	17.1	$\begin{array}{c c} 16 \cdot 3 \\ 2 \cdot 2 \end{array}$		$35.0 \\ 1.4$	45·2 1·6	$\begin{array}{c} 31.7 \\ 2.3 \end{array}$
In $CH_3OH^{\dagger} \phi_0$	$\begin{vmatrix} -3.8 \\ 9.2 \end{vmatrix}$	-3.3 11.4	(5.2)?	$\frac{11.8}{12.0}$	$\frac{21.9}{10.8}$	

In methyl alcohol the apparent molar volumes of salts are considerably less than in water, and in some cases become negative in very dilute solutions. In such a case, when the salt is added to the methyl alcohol the total volume of the solution is less than the original volume of the solvent. It is therefore evident that the solvent has undergone a contraction as the result of the presence of the ions. A contraction also occurs in aqueous solutions, though less clearly marked. For example, at 18° the molar volume of solid lithium chloride is 20.5 c.c., and its partial molar volume at m=1 is 18.6 c.c.

In the intense electric fields near the ions very considerable pressures are produced in the solvent which are sufficient to cause an appreciable contraction. T. J. Webb has given a somewhat elaborate calculation of the contraction or electrostriction produced in this way.‡ Table XVI. gives the pressures in megadynes/cm.² at various distances r from the centre of a univalent ion

^{*} Geffcken, Z. physikal. Chem., 155, 1, 1931.

[†] Vosburgh, Connell and Butler, J. Chem. Soc., p. 933, 1933.

[‡] J. Amer. Chem. Soc., 48, 2589, 1926.

in water and methyl alcohol, as calculated by Webb's equations * (which refer to infinite dilution), and also the fractional contraction of the solvent, which is given as $-\Delta V_r/V$, where ΔV_r is the change of volume of a small mass of the solvent at the distance r, and V the final volume. The total contraction produced by a gm. molecule of ions of radius r_0 is given by the integral

$$C = N_0 \int_{r_0}^{\infty} - (\Delta V_r / V) \, 4\pi r^2 \, . \, dr.$$

TABLE XVI.

WATER.

r, Å.	4.26	3.24	2.50	$2 \cdot 13$	1.71	1.25	1.00
p_{i}	26	169	713	1470	3520	11500	39100
$-\Delta V_r/V$	0.012	0.064	0.196	0.301	0.456	0.729	1.151
C, c.c.	1.97	5.0	10.4	14.1	18.3	22.8	25.6

METHYL ALCOHOL.

r, Å.	4.47	3.44	2.61	2.20	1.75	1.27	0.91
p_r	35.7	220	640	1290	3060	9160	36400
$-\Delta V_r/V$	0.034	0.140	0.268	-0.377	0.565	0.905	1.60
C, e.e.	$7 \cdot 6$	15.8	27.6	$33 \cdot 2$	$39 \cdot 1$	44.8	49.4

The apparent molar volume is obtained by adding the intrinsic volumes of the ions themselves, viz.

$$N_0\,.\,4\pi/3\,.\,r_0{}^3.$$

The following table gives the mean radii of the ions of several salts which are required to give agreement of the observed with the calculated values of ϕ_0 .

^{*} Vosburgh, Connell and Butler, loc. cit.

TABLE XVII.

MEAN ATOMIC RADII OF IONS FROM APPARENT
MOLAR VOLUMES

Salt.	LiCl.	NaCl.	KCl.	NaI.	KI.
Mean radius, Å, H ₂ O -	2.09	2.08	2.19	2.28	2.38
Mean radius, Å, CH ₃ OH	2.28	2.29	2.37	2.43	2.51

The fact that the radii required in the two solvents approximate to each other may be taken as evidence that the contraction is mainly electrostatic in origin.* It can be seen from Table XVI. that the pressures at a given distance in the two solvents are not very different, and the greater contraction in methyl alcohol arises from its greater compressibility.

The slope a (Table XV.) for uni-univalent salts in methyl alcohol is approximately six times that in water. This is also in accordance with Redlich and Rosenfeld's equation (183), for taking $D = D_0(1 + 1 \cdot 0 \times 10^{-4}P)$, $\beta = 1 \cdot 2 \times 10^{-4}$, we obtain a = 14, which is in reasonable agreement with the observed values. It must be noted, however, that while according to Redlich and Rosenfeld's equation all uni-univalent salts should have the same value of a in a given solvent, the observed values of a in both water and methyl alcohol certainly differ among themselves by more than the experimental error. It must be remembered that the Debye-Hückel limiting equation, which is the basis of the calculation, is only valid in extremely dilute solutions—in fact at lower concentrations than those at which the accurate measure-

^{*} These radii are, however, considerably greater than those derived from measurements of crystals. It is probable that Webb's theory requires some modification in respect to the water molecules which are in actual contact with the ions.

ment of apparent molar volumes is feasible. It is surprising that the relation $\phi = \phi_0 + a\sqrt{c}$ holds over a much more extensive concentration range than the equation $\log f_+ = -B\sqrt{2c}$, from which the former can be derived.

A more complete equation for \overline{V}_2 would be obtained by differentiating with respect to the pressure the complete Debye-Hückel expression:

$$\log f_{\pm} = -rac{B\sqrt{2c}}{1+Aar{r}\sqrt{2c}} + C$$
 , $2c$.

The pressure variation of C is unknown, but the fact that $\phi = \phi_0 + a\sqrt{c}$ holds in many cases even in concentrated solutions indicates that it is probably negligible. That this should be so can readily be understood, for C depends upon the interaction of the ions and the solvent in the region where the pressure due to the electric field is extremely high and the effect of a small increase in the applied pressure will therefore be small. The variations in the actual value of a might be accounted for if the ionic radius term $A\tilde{r}$ were taken into account.

Heats of Dilution of Strong Electrolytes. By (141),

$$\begin{bmatrix} d(\frac{\bar{F}_2 - \bar{F}_2^\circ}{T}) \\ dT \end{bmatrix}_{P, m} = -\frac{\bar{H}_2 - \bar{H}_2^\circ}{T^2},$$

where \bar{F}_2 , \bar{H}_2 are the partial free energy and heat content in a given solution, and \bar{F}°_2 , \bar{H}°_2 the corresponding values in the standard state $(f_2=1)$. For dilute solutions the partial free energy of a uni-univalent strong electrolyte, according to the Debye-Hückel limiting equation, is

$$\boldsymbol{\bar{F}}_2 - \boldsymbol{\bar{F}^{\circ}}_2 = 2RT\log m - 2 \times RT$$
 . $B\sqrt{2c},$

and therefore (since m is independent of the temperature),

$$\left[\frac{d(2B\sqrt{2c})}{dT}\right]_{P,\,m} = \frac{\bar{H}_2 - \bar{H}^\circ_{\ 2}}{RT^2} = \frac{\Delta \bar{H}_2}{RT^2}.$$

Differentiating with respect to the temperature (at constant P), we have

$$\frac{d(B\sqrt{2c})}{dT} = \frac{dB}{dT}\sqrt{2c} + B\frac{d(\sqrt{2c})}{dT},$$
 and
$$\frac{dB}{dT} = -\frac{3}{2} \cdot \frac{B}{T} \left[1 + \frac{T}{D} \left(\frac{dD}{dT} \right) \right]$$
 and
$$\frac{d\sqrt{2c}}{dT} = -\frac{1}{2}\sqrt{2c} \cdot \frac{1}{V} \left(\frac{dV}{dT} \right)_{P},$$

where V=1/c is the volume of solvent containing 1 mol of the salt, and $1/V\left(\frac{dV}{dT}\right)_P$ can for dilute solutions be taken as the coefficient of thermal expansion of the solvent at constant pressure. Therefore

$$\left[\frac{d(B\sqrt{2c})}{dT}\right]_{P,\,m} = -\frac{3}{2}\,\,\frac{B}{T}\bigg[1 + \frac{T}{D}\binom{dD}{dT}_P + \frac{T}{3\,\overline{V}}\binom{dV}{dT}_P\bigg]\sqrt{2c},$$

and therefore

$$\Delta \bar{H}_2 = -3RT \cdot B \left[1 + \frac{T}{D} \left(\frac{dD}{dT} \right)_P + \frac{T}{3V} \left(\frac{dV}{dT} \right)_P \right] \sqrt{2c} \cdot * \quad (184)$$

This gives the partial molar heat content of the salt in the given solution (i.e. the heat content change in the transfer of the salt from an infinitely dilute solution to the given solution, per mol). The total heat content of the given solution, taking the heat contents of the pure solvent and of the salt at infinite dilution as zero, can easily be shown to be $2/3\Delta \bar{H}_2$, and this is equal to the heat evolved when a quantity of the solution containing

^{*} An equivalent expression containing the first two terms in the square bracket was obtained by Bjerrum (*Z. physikal. Chem.*, 109, 145, 1926). The third term was added by Gatty (*Phil. Mag.*, 11, 1082, 1931) and a little later by Scatchard (*J. Amer. Chem. Soc.*, 53, 2037, 1931).

a mol of the salt is diluted with an infinite volume of the pure solvent. The heat of an infinite dilution is thus equal to

 $Q_e^{\infty} = 2RT \cdot B \left[1 + \frac{T}{D} \left(\frac{dD}{dT} \right)_P + \frac{T}{3V} \left(\frac{dV}{dT} \right)_P \right] \sqrt{2c}. \quad (185)$

Writing $Q_c^{\infty} = b\sqrt{c}$, the value of b calculated by (185), taking $1 + \frac{dD}{D} \cdot \left(\frac{dD}{dT}\right)_P = -0.379$, is 492 for uni-univalent salts in water at 25°. Lange and Leighton * found for KCl solutions the limiting value b = 376, which differs appreciably from that calculated. The temperature

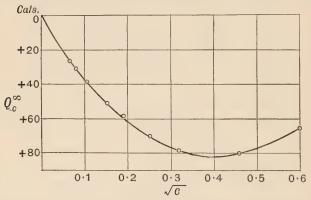


Fig. 19.—Heat of infinite dilution of KCl solutions (Lange and Leighton).

coefficient of the dielectric constant of water is, however, not known with certainty, and the discrepancy may be due to the inaccuracy of the value employed. In more concentrated solutions considerable deviations from the limiting equation occur,† the nature of which is shown in Fig. 19.

^{*} Z. f. Electrochem., 34, 566, 1928.

[†] See Lange and Robinson, Chemical Reviews, 9, 89, 1931.

CHAPTER VII

IONIC EQUILIBRIA IN SOLUTION AND SALTING-OUT

Electrical Conductivity of Solutions of Strong Electrolytes. The conductivity of a solution depends on the number of ions it contains and on their mobility. In the Arrhenius theory it was assumed that the mobility was independent of the concentration, and variations in the molecular conductivity were ascribed to changes in the number of ions. Debye and Hückel, in their second paper,* made a calculation of the effect of the interionic forces on the mobility of ions. In their calculation of the partial free energy of ions the central ion was supposed to be at rest, and the ionic atmosphere was symmetrical round about it, but if the ion is in motion under the influence of a potential gradient in the solution, the ionic atmosphere will no longer be symmetrical. The formation and disappearance of the atmosphere occupies a finite time which Debye and Hückel expressed in terms of a quantity τ called the time of relaxation. τ is approximately equal to the time in which the effective radius of the ionic atmosphere becomes twice its original value when the central ion is suddenly removed. For a uniunivalent electrolyte it is given by

 $\tau = \rho/\kappa^2 kT$,

* Physikal. Z., 24, 305, 1923.

where ρ is the frictional constant of an ion, defined as the force opposing an ion moving with unit velocity. For a tenth normal solution of KCl in water at 25°, $\tau = 0.55 \times 10^{-9}$ seconds.

When an ion is moving through the solution the atmosphere in front of it has to be built up continuously, while the atmosphere behind dies away. On account of the finite time of relaxation the atmosphere in front of the ion never reaches its equilibrium density, while that behind is always a little greater than the equilibrium value. Consequently the average centre of charge of the ionic atmosphere is always a little behind the ion, and since the total charge of the ionic atmosphere is equal and opposite to that of the ion the motion of the latter will be retarded. The actual amount of dissymmetry, which is proportional to the velocity of the ion, is small, but on account of the relatively large electronic charge it produces an appreciable retardation of the ion.

The ionic atmosphere also influences the ionic mobility because of the increased viscous resistance caused by the movement of the ionic atmosphere with the ion. Taking both these effects into account Debye and Hückel obtained the equation

$$\frac{\Lambda_0-\Lambda_c}{\Lambda_0} = \left\{\frac{k_1}{(DT)^{3/2}} \cdot w_1 + \frac{k_2}{(DT)^{1/2}} \cdot w_2 b\right\} \sqrt{2c},$$

where Λ_0 , Λ_c are the molecular conductivities at infinite dilution, and in the solution of concentration c; k_1 , k_2 universal constants, w_1 , w_2 valency factors, and b the average radius of the ions. The first term on the right expresses the result of the dissymmetry of the ionic atmosphere; the second, which they called the cataphoretic term, the result of the motion of the ionic

atmosphere. This equation is evidently equivalent to Kohlrausch's empirical equation * $\Lambda = \Lambda_0 - x\sqrt{c}$, which fits the results for very dilute solutions of strong electrolytes in water and similar solvents with considerable accuracy (Fig. 20).

It was pointed out by Onsager † that in calculating the dissymmetry term Debye and Hückel had assumed the uniform motion of the ion under the applied field, and that if the Brownian movement of the ion is taken into account a factor $(2-\sqrt{2})$ is introduced. He also showed that the mean radius of the ions could be eliminated from the equation, which was then obtained in the form

$$\Lambda_c = \Lambda_0 - \left[\frac{0.986 \times 10^6}{(DT)^{3/2}} (2 - \sqrt{2}) z^2 \Lambda_0 + \frac{58 \cdot 0z}{(DT)^{1/2} D} \right] \sqrt{2}zc \tag{186}$$

for a z-valent binary electrolyte. For uni-univalent electrolytes in water at 25° this reduces to

$$\Lambda_c = \Lambda_0 - (0.228\Lambda_0 + 59.8)\sqrt{c}.$$

Comparing the values of x in the Kohlrausch equation with those calculated by equation (186), he found good agreement for uni-univalent salts in aqueous solution, the average deviation being only 7%. On the other hand in the case of bi-bivalent salts the experimental values of x are often considerably greater than the calculated values. While agreement of the experimental with the calculated value of x must be regarded as good evidence for the complete dissociation of the salt, when the observed value is considerably greater than the theoretical (i.e. the observed molecular conductivity falls off with increase of concentration more rapidly than that

^{*} Z. f. Electrochemie, 13, 333, 1907.

[†] Physikal. Z., 27, 388, 1926; 28, 277, 1927.

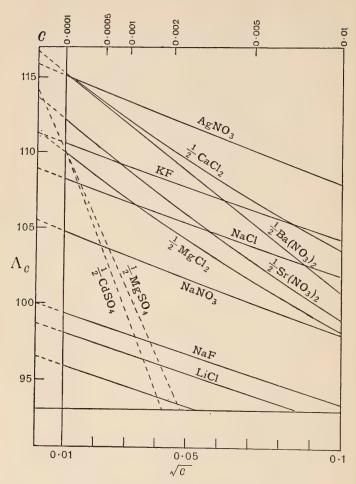


Fig. 20.—Part of Kohlrausch's diagram. Λ_c at 18° plotted against \sqrt{c} , for aqueous solutions of salts.

calculated), it is probable that the salt is incompletely dissociated. The degree of dissociation may be determined by $\gamma = \Lambda_c/\Lambda'$, where Λ' is the conductivity calculated by the Onsager equation for the given concentration. The Onsager equation gives such good agreement with many uni-univalent salts that in cases of nonagreement considerable reliance may be placed upon the degree of dissociation calculated in this way. It is necessary to state, however, that the Onsager equation applies only to very dilute solutions ($\sqrt{c} < 0.02$). In concentrated solutions other factors enter which have not been elucidated.

Numerous determinations of the conductivities of salts in non-aqueous solvents have been made. Hartley and his co-workers in particular have made measurements of a large number of salts in methyl and ethyl alcohols and in other solvents. In methyl alcohol * they found that while all uni-univalent salts obey the square root relation and in many cases the experimental values of x agree well with those calculated by the Onsager equation, the individual differences were often greater than in the case of water. In ethyl alcohol, also, all uni-univalent salts obey the square root relation, but the observed and calculated values of x differ to a somewhat greater extent than in methyl alcohol. A greater variety of behaviour in these solvents is shown by acids (Fig. 21).† Hydrochloric, perchloric, ethyl sulphuric and benzenesulphonic acids are strong acids in water and both alcohols. The deviation from Onsager's equation, indicating lack of complete dissociation, is greatest in ethyl alcohol.

^{*} Proc. Roy. Soc., A, 109, 351, 1925; 127, 228, 1930; J. Chem. Soc., 2488, 1930.

[†] Murray-Rust and Hartley, Proc. Roy. Soc., A. 126, 84, 1929.

Nitric and thiocyanic acids, which are strong acids in water, are weak in ethyl alcohol, while iodic acid, which

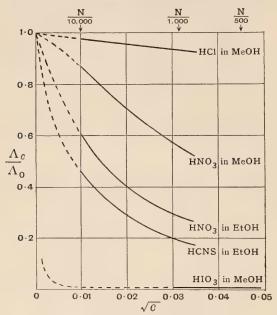


Fig. 21.—Electrical conductivities of acids in methyl and ethyl alcohols (Murray-Rust and Hartley).

is not completely dissociated in aqueous solution, is weak in methyl alcohol, having a dissociation constant about 10^{-8} .

Salts of a higher valence type, particularly salts of metals of the transitional series, are often incompletely ionised in these solvents. For example, cadmium and mercuric chlorides are incompletely ionised even in water and are weaker electrolytes in methyl alcohol. Zinc chloride, although a strong electrolyte in water,

is incompletely ionised in methyl alcohol and is scarcely ionised at all in ethyl alcohol.

In non-hydroxylic solvents such as nitromethane, acetonitrile, nitrobenzene, acetone, a much greater variety of behaviour is encountered and even uniunivalent salts are in some cases weak electrolytes. In general it is found that salts are much less completely dissociated in these solvents than in the hydroxylic solvents mentioned above. This is not due solely to differences of dielectric constant, since nitromethane, nitrobenzene and acetonitrile all have greater dielectric constants than methyl alcohol. It has to be admitted that the dissociation of electrolytes is not determined solely by the dielectric constant of the medium. The chemical nature of the latter plays an important part, the nature of which is at present largely unknown.

True Dissociation Constant of a Weak Electrolyte. Consider a weak acid which dissociates as $HX = H^+ + X^-$. The partial free energies of HX, H^+ , X^- can be represented by the following equations:

$$\begin{split} & \bar{F}_{\,\mathrm{H}^{+}} \! = \! \bar{F}^{\circ}_{\,\mathrm{H}^{+}} + RT \log \, \alpha_{\mathrm{H}^{+}}, \\ & \bar{F}_{\,\mathrm{X}^{-}} \! = \! \bar{F}^{\circ}_{\,\mathrm{X}^{-}} + RT \log \, \alpha_{\mathrm{X}^{-}}, \\ & \bar{F}_{\,\mathrm{HX}} \! = \! \bar{F}^{\circ}_{\,\mathrm{HX}} \! + \! RT \log \, \alpha_{\mathrm{HX}}. \end{split}$$

Since for equilibrium $\bar{F}_{\rm HX} = \bar{F}_{\rm H^+} + \bar{F}_{\rm X^-}$, we have

or

$$\log \frac{\alpha_{H^{+}} \cdot \alpha_{X^{-}}}{\alpha_{HX}} = \frac{\bar{F}^{\circ}_{HX} - \bar{F}^{\circ}_{H^{+}} - \bar{F}^{\circ}_{X^{-}}}{RT},$$

$$\frac{\alpha_{H^{+}} \cdot \alpha_{X^{-}}}{\alpha_{HX}} = K. \qquad (187)$$

K is the true dissociation constant of the acid, and its value in a given solvent is thus fixed by the values of $\bar{F}^{\circ}_{\mathbf{H}^{+}}$, $F^{\circ}_{\mathbf{X}^{-}}$ and $\bar{F}^{\circ}_{\mathbf{H}\mathbf{X}}$.

The Ostwald dissociation constant was defined as

$$K = \frac{c_{\mathrm{H}^+} \cdot c_{\mathrm{X}^-}}{c_{\mathrm{HX}}} = \frac{\gamma^2 c}{1 - \gamma},$$

where c is the total concentration of the acid and γ its degree of dissociation, which was determined by the Arrhenius expression $\gamma = \Lambda/\Lambda_0$. Two corrections are required in this calculation.* In the first place, the variation of the mobilities of the ions with their concentration must be taken into account in finding the degree of dissociation. Instead of $\gamma = \Lambda/\Lambda_0$, we must use $\gamma = \Lambda/\Lambda_e$, where Λ_e is the sum of the equivalent conductivities of the ions at their actual concentration. can be obtained by $\Lambda_e = \Lambda_0 - x \sqrt{\gamma c}$, where the constant x is given by Onsager's equation. Since γ is initially unknown, in the first instance the value of γ given by Λ/Λ_0 can be used, and from it a new value of $\gamma = \Lambda/\Lambda_a$ is then obtained. A short series of approximations of this kind is sufficient to fix the corrected value of γ . Secondly, in finding the dissociation constant it is necessary to use activities instead of concentrations. Since very small concentrations of ions will not appreciably affect the activity of a neutral molecule, it can be assumed that the activity of the undissociated part of the acid is the same as its concentration. We can then write (187) as

$$\frac{c_{\rm H^+} \cdot c_{\rm X^-} \cdot f_{\rm H^+} \cdot f_{\rm X^-}}{c_{\rm H\,X}} = K,$$

where $f_{\rm H^+}$, $f_{\rm X^-}$ are the activity coefficients of the ions. These can be calculated by the Debye-Hückel limiting expression

 $\log(f_{\rm H^+} \cdot f_{\rm X^-}) = -2B\sqrt{c_i}$.

* First made by Noyes and Sherrill, J. Amer. Chem. Soc., 48, 1861, 1926; MacInnes, ibid., 48, 2068, 1926.

We thus obtain

$$\log\left(\frac{c_{\mathrm{H}^{+}} \cdot c_{\mathrm{X}^{-}}}{c_{\mathrm{HX}}}\right) = \log\left(\frac{\gamma^{2}c^{2}}{(1-\gamma)c}\right) = \log K + 2B\sqrt{c_{i}}, \quad (188)$$

where c is the total concentration of the acid, γ the true degree of dissociation and c_i the sum of concentrations of the ions. The following table gives the data of MacInnes and Shedlovsky* for acetic acid, as calculated by C. W. Davies.†

TABLE XVIII.

Dissociation of Acetic Acid at 25° in Aqueous Solution.

$$\Lambda_e = 390.59 - 148.61 \sqrt{\gamma c}.$$

$c \times 10^3$.	φ Λ.	$\gamma c imes 10^3$.	$\gamma^2 c^2/1 - \gamma c$
0.02801	210.32	0.01511	1.7682
0.11135	127.71	0.03649	1.7787
0.15321	112.02	0.04405	1.7775
0.21844	96.466	0.05410	1.7810
1.02831	48.215	0.12727	1.7974
1.36340	42.215	0.14803	1.8030
2.41400	$32 \cdot 208$	0.20012	1.8090
3.44065	$27 \cdot 191$	0.24092	1.8140
5.91153	20.956	0.31929	1.8230

The values of $\log(\gamma^2 c^2/1 - \gamma c)$ are plotted against $\sqrt{c_i}$ in Fig. 22. They are in good agreement with the straight line, having the slope 1.01 which is the value of 2B in (188), according to Debye and Hückel. The value of K, which is given by the intercept made by this line on the axis at zero concentration, is equal to 1.753×10^{-5} .

Determination of the Dissociation Constant of a Weak Acid by Electromotive Force Measurements. Galvanic

^{*} J. Amer. Chem. Soc., 54, 1429, 1932.

[†] Conductivity of Electrolytes, 2nd ed., p. 105.

cells have been devised by Harned and his co-workers * by means of which the dissociation constants of weak

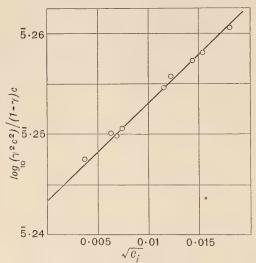


Fig. 22.—Apparent dissociation constants of acetic acid in aqueous solution (Davies).

acids and bases can be determined. For example, the dissociation constant of acetic acid (HAc) can be determined by means of the cell

$$\mathbf{H_2} \, \big| \, \mathbf{HAe}(m_1), \ \mathbf{NaAe}(m_2), \ \mathbf{NaCl}(m_3), \ \mathbf{AgCl}(s) \, \big| \, \mathbf{Ag}.$$

Since the cell reaction is $\frac{1}{2}H_2 + AgCl(s) = Ag + HCl$, the electromotive force is determined by the activity of hydrogen chloride in the solution and is given by

$$E = E_0 - \frac{RT}{F} \log f_{H^+} f_{\text{Cl}} - m_{H^+} m_{\text{Cl}}, \dots (189)$$

*Harned and Robinson, J. Amer. Chem. Soc., 50, 3157, 1928; Harned and Owen, *ibid.*, 52, 5079, 1930; Harned and Ehlers, *ibid.*, 54, 1350, 1932.

where E_0 is the electromotive force of a cell made of similar electrodes in a solution containing hydrochloric acid of unit activity. This can be determined by measurements of the cell

$$H_2 \mid HCl(m), AgCl(s) \mid Ag,$$

according to which E_0 has the value 0·22239 at 25°. We may substitute for $f_{\rm H^+}m_{\rm H^+}$ in (189) by means of

and we obtain

$$E - E_0 + \frac{RT}{F} \log \frac{m_{\text{HAc}} m_{\text{Cl}^-}}{m_{\text{Ac}^-}}$$

$$= -\frac{RT}{F} \log \frac{f_{\text{H}^+} f_{\text{Cl}^-} \cdot f_{\text{HAc}}}{f_{\text{H}^+} f_{\text{AC}^-}} - \frac{RT}{F} \log K \dots (190)$$

All the quantities of the left side of this equation are known.* The first term on the right becomes zero at infinite dilution, so that if the values of the left side of the equation are extrapolated to infinite dilution we obtain $RT/F \log K$. This extrapolation can be made by plotting the left side of the equation against the ionic strength of the solution, since in dilute solutions both $\log(f_{\rm H^+}f_{\rm Cl^-}/f_{\rm H^+}f_{\rm Ac^-})$ and $\log f_{\rm HCl}$ vary linearly with the total ionic concentration. In this way Harned and Ehlers found that the value of K for acetic acid at 25° is 1.754×10^{-5} , which is in excellent agreement with the corrected value derived from conductivity measurements.

Dissociation Constant and Degree of Dissociation of Water. The dissociation of water may be represented by the equation, $H_2O=H^++OH^-$. The partial free

^{*} $m_{\text{Cl}^-} = m_3$, $m_{\text{Ac}^-} = m_2 + m_{\text{H}^+}$, $m_{\text{HAc}} = m_1 - m_{\text{H}}$, where m_{H^+} is the concentration of hydrogen ions formed by the dissociation of acetic acid.

energies of water and of the hydrogen and hydroxyl ions may be expressed by

$$\begin{split} & \bar{F}_{\mathrm{W}} = & \bar{F}^{\circ}_{\mathrm{W}} + RT \log \alpha_{\mathrm{W}}, \\ & \bar{F}_{\mathrm{OH^{-}}} = & \bar{F}^{\circ}_{\mathrm{OH^{-}}} + RT \log \alpha_{\mathrm{OH^{-}}}, \\ & \bar{F}_{\mathrm{H^{+}}} = & \bar{F}^{\circ}_{\mathrm{H^{+}}} + RT \log \alpha_{\mathrm{H^{+}}}; \end{split}$$

where $a_{\rm W}$ is taken as unity in pure water, and $a_{\rm OH^-}$, $a_{\rm H^+}$ are made equal to the ionic concentrations $m_{\rm H^+}$, $m_{\rm OH^-}$ in solutions which contain very small concentrations of these and of other ions. Since $\bar{F}_{\rm W} = \bar{F}_{\rm OH^-} + \bar{F}_{\rm H^+}$, it follows that

$$a_{\text{H}} + a_{\text{OH}} - /a_{\text{W}} = K_{\text{W}}, \dots (191)$$

$$\log K_{\text{W}} = \frac{\bar{F}^{\circ}_{\text{H}^{+}} + \bar{F}^{\circ}_{\text{OH}^{-}} - \bar{F}^{\circ}_{\text{W}}}{P^{T}}.$$

where

 $K_{\rm W}$ is the true dissociation constant of water. In order to evaluate it, it is necessary to determine the three quantities $a_{\rm H^+}$, $a_{\rm OH^-}$ and $a_{\rm W}$ in the same solution. Harned and his co-workers have devised methods of determining these quantities by means of reversible galvanic cells without liquid junctions. Their first method involved the use of amalgam electrodes.* Later they devised a simpler method, of which the following is an example.† Consider the cell

$$H_2 \mid KOH(m_0), KCl(m), AgCl(s) \mid Ag. \dots (A)$$

* Harned, J. Amer. Chem. Noc., 47, 930, 1925; Harned and Swindells, *ibid.*, 48, 126, 1926; Harned and James, J. Physical Chem., 30, 1060, 1926.

† Harned and Schupp, J. Amer. Chem. Soc., 52, 3892, 1930; Harned and Mason, ibid., 54, 3112, 1932; Harned and Hamer, ibid., 55, 2194, 1933; Harned and Capson, ibid., 55, 2206, 1933.

Since the electromotive force is determined by the activity of hydrogen chloride in the solution, we have

$$E_{\rm A} = E_0 + \frac{RT}{zF} \log f_{\rm H^+} f_{\rm Cl^-} m_{\rm H^+} m_{\rm Cl^-}, \dots (192)$$

where E_0 is the electromotive force of a cell made of similar electrodes in a solution containing hydrochloric acid of unit activity.

We can substitute for $f_{\rm H^+}$ $m_{\rm H^+}$ in (192) by means of the equation $K_{\rm W}$ = $f_{\rm H^+}$ $f_{\rm OH^-}$ $m_{\rm H^+}$ $m_{\rm OH^-}/a_{\rm W}$, and we thus obtain

$$E - E_0 + \frac{RT}{zF} \log \frac{m_{\text{Cl}^-}}{m_{\text{OH}^-}} = \frac{RT}{zF} \log \frac{f_{\text{H}^+}f_{\text{OH}^-}}{\alpha_{\text{W}}} - \frac{RT}{zF} \log K_{\text{W}} - \frac{RT}{zF} \log f_{\text{H}^+}f_{\text{Cl}^-}.$$
(193)

The activity coefficients of the ions $f_{\rm H^+}$, $f_{\rm OH^-}$, $f_{\rm Cl^-}$ all become unity when the salt concentration becomes very small and $\alpha_{\rm W}$ also becomes equal to unity in pure water. The quantity on the left of this equation therefore becomes equal to $RT/zF\log K_{\rm W}$ at zero salt concentration. Harned plots this quantity against the ionic strength of the solution, and a short extrapolation to $\mu=0$ gives the value of $RT/zF\log K_{\rm W}$. In this way it is found that the value of $K_{\rm W}$ at 25° is $1.008\pm0.001\times10^{-14}$.

Since $K_{\rm W}=f_{\rm OH^-}f_{\rm H^+}$, $m_{\rm H^+}m_{\rm OH^-}/a_{\rm W}$, it follows that the ionic product of the concentrations $m_{\rm H^+}m_{\rm OH^-}$ increases as $f_{\rm OH^-}f_{\rm H^+}$ decreases. In dilute solutions the activity coefficients of the hydrogen and hydroxyl ions, like those of other ions, decrease with increasing ionic strength of the solution and the ionic concentration product therefore increases. The extent of this increase can be calculated in very dilute solutions by means of the Debye-Hückel limiting expression. In such solutions we have by (171), $\log (f_{\rm H^+}f_{\rm OH^-}) = -2B\sqrt{\Sigma c_i z_i^2}$, and taking a as unity it follows that $\log (m_{\rm H^+}m_{\rm OH^-}) = \log K_{\rm W} + 2B\sqrt{\Sigma c_i z_i^2}$.

In concentrated solutions the activity coefficients of the H⁺ and OH⁻ ions will be influenced specifically by the nature of the other ions present in the solution. The value of $f_{\rm H^+}f_{\rm OH^-}/a_{\rm W}$ can, however, be determined experimentally from (193) if we know $f_{\rm H^+}f_{\rm Cl^-}$.

The determination of this quantity in barium chloride solutions may be quoted as an example. The activity coefficients of HCl in BaCl₂ solutions can be determined (see p. 137) by cells of the type

$$H_2 \mid HCl(m_1)$$
, $BaCl_2(m_2)$, $AgCl \mid Ag$.

It has been pointed out that when the concentration of hydrogen chloride is very small, its activity coefficient depends only on the nature and concentration of the solution in which it is dissolved and not on its concentration (m_1) . In a mixed solution of $\operatorname{Ba}(\operatorname{OH})_2(m_0)$ and $\operatorname{BaCl}_2(m_2)$ it can be assumed if m_0 is small that the activity coefficient of hydrogen chloride is the same as in a pure barium chloride solution of the same total ionic strength. In Table XIX the second column gives

the values of $E-E_0+0.05915\log\frac{m_{\rm Cl^-}}{m_{\rm OH^-}}$ determined from the cells

$$\mathbf{H_2} \mid \mathrm{Ba}(\mathrm{OH})_2(m_0), \ \mathrm{BaCl}_2(m_2), \ \mathrm{AgCl}(s) \mid \mathrm{Ag}.$$

The third column gives the activity coefficients of HCl in these solutions and the fourth the calculated values of $f_{\rm H^+}f_{\rm OH^-}/\alpha_{\rm W}$. When the activity of water is known it is thus possible to find the products of the activities of the hydrogen and hydroxyl ions $f_{\rm H^+}f_{\rm OH^-}$ which are given in the fifth column. Finally, the ionic concentration product of water can be determined by $m_{\rm H^+}m_{\rm OH^-}=K_{\rm W}\,\alpha_{\rm W}/f_{\rm H^+}f_{\rm OH^-}$. Values of $m_{\rm W}=\sqrt{m_{\rm H^+}m_{\rm OH^-}}$

are given in the last column. Fig. 23 shows the values of this quantity in a number of chloride solutions.

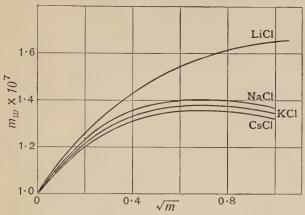


Fig. 23.—Dissociation of water in some salt solutions (Harned and Schupp).

TABLE XIX.

ACTIVITY COEFFICIENT PRODUCT AND DISSOCIATION OF WATER IN BARIUM CHLORIDE SOLUTIONS AT 25°.

 $\mathbf{H_2}\mid \mathrm{Ba}(\mathrm{OH})_2(m_0),\ \mathrm{BaCl}_2(m),\ \mathrm{AgCl}(s)\mid \mathrm{Ag}.$

μ.	$ \begin{vmatrix} E - E_0 \\ + 0.05915 \log m / m_0. \end{vmatrix} $	f _H +f _{C1}	$f_{\mathrm{H}^+}f_{\mathrm{OH}^-}/\alpha_{\mathrm{W}}$.	$f_{\mathrm{H}^+}f_{\mathrm{OH}^-}$.	$mW \times 10^7$
0.01	0.8279	9.891	0.792	0.793	1.13
0.05	0.8276	0.818	0.660	0.659	1.23
0.1	0.8272	0.776	0.582	0.581	1.31
0.2	0.8264	0.739	0.514	0.512	1.40
0.5	0.8242	0.702	0.426	0.423	1.54
1.0	0.8210	0.699	0.373	0.368	1.64
1.5	0.8180	0.713	0.345	0.337	1.71
2.0	0.8154	0.737	0.335	0.325	1.73
3.0	0.8104	0.825	0.343	0.325	1.71
4.0	0.8069	0.934	0.384	0.355	1.62

The Salting out of Non-Electrolytes. In many cases the partial free energy of a non-electrolyte in aqueous solution is increased by the addition of salts. The following are a few examples of cases in which this phenomenon occurs. (1) The partial pressure of volatile solutes, such as ethyl alcohol in dilute solution, is increased by salts. (2) The solubility of gases at constant pressure is usually less in salt solutions than in water. (3) The solubility of solids, e.g. iodine,* is decreased by salts. Since the partial free energy of the solid is the same in all saturated solutions, this means that the saturation value is reached at a smaller concentration in the presence of a salt, i.e. the partial free energy of the solute at constant concentration is increased by the salt. (4) The presence of salts also often reduces the mutual miscibility of partially miscible liquids. The addition of a salt to a saturated solution of ether may cause its separation into two layers. † (5) When the distribution of a solute such as acetic acid between aqueous solutions and a nearly immiscible solvent like amyl alcohol (which does not dissolve salts to any appreciable extent) is studied, it is found that the distribution ratio $c_{\text{(water)}}/c_{\text{(alcohol)}}$ is decreased in most cases by the addition of salts to the aqueous solution. ‡ (6) The depression of the freezing point produced by a salt and a non-electrolyte together is greater than the sum of the depressions produced by each singly at equivalent concentrations.§

If \bar{F}_2 is the partial free energy of a non-electrolyte in

^{*} Carter, J. Chem. Soc., 127, 2861, 1925.

[†] Thorne, ibid., 119, 262, 1921.

[‡] J. N. Sugden, J. Chem. Soc., p. 174, 1926.

[§] Tammann and Abegg, Z. physikal. Chem., 9, 108, 1892; 11, 259, 1893.

dilute aqueous solution of concentration m_2 , we may write

 $\bar{F}_2 = \bar{F}_2^{\circ} + RT \log m_2 f_2; \dots (194)$

and if \bar{F}_{2} is its partial free energy in a similar solution containing a salt at the concentration m, we have

$$\bar{F}_{2}' = \bar{F}_{2} + RT \log m_{2} f_{2}'. \dots (195)$$

The change in the partial free energy of the nonelectrolyte produced by the salt is thus

$$\bar{F}_{2}' - \bar{F}_{2} = RT \log(f_{2}'/f_{2}).$$

It has been found that this quantity varies approximately linearly with the salt concentration, i.e.

$$\log (f_2'/f_2) = km_3.$$
(196)

This relation was first observed by V. Rothmund,* in his studies of the effect of salts on the solubilities of sparingly soluble non-electrolytes.

A theory of the salting-out effect has been given by Debye and McAulay.† It has already been pointed out that the molecules of a polarisable solvent are strongly attracted by the intense electric fields in the vicinity of ions. If the solution contains "solvent" molecules of two kinds, the more polarisable ones will be more strongly attracted and will tend to congregate round the ions. Near the ions there will thus be a greater proportion of the more polarisable molecules than in the bulk of the solution, and the proportion of the less polarisable molecules in the solution at a distance from the ions will be increased. The activity of the less polarisable molecules

^{*} Z. physikal. Chem., 33, 401, 1900; 69, 523, 1909; cf. Setschenov, ibid., 4, 117, 1889.

[†] Physikal, Z., 26, 22, 1925; see also McAulay, J. Physical Chem., 30, 1202, 1926; Debye, Z. physikal. Chem., 30, 56, 1927.

in the solution will thus be increased by the presence of ions, and the effect will be approximately proportional to the number of ions present. Water, on account of its high dielectric constant, is much more polarisable than most organic substances, and these are "salted out" in aqueous solutions. The reverse should be the case, however, with solutes which are more polarisable than water. This has been confirmed with aqueous solutions of hydrocyanic acid, which is "salted in", i.e. its partial free energy is decreased by the presence of salts.*

*The quantitative calculation of the effect of a salt on the partial free energy of a non-electrolyte is somewhat difficult. Debye and McAulay gave an indirect calculation which depended on evaluating the electric energy of the solution, taking into account the lowering of the dielectric constant produced by the non-electrolyte, and then separating the partial free energy of the latter. A more direct derivation of a similar equation was given by Butler.†

According to simple electrostatic theory, the field strength at a distance r from the centre of a spherical ion of charge e is $E = -e/Dr^2$. The electric work done in bringing a molecule B from infinity to a point near the ion where the field strength is E is $\int_0^E P_B \cdot \delta v_B \cdot dE$, where P_B is the polarisation produced in unit volume of B by the field and δv_B the volume of the molecule.‡ The polarisation is the electric moment produced in a medium by the action of an electric field, either by the orientation of the permanent dipoles or by induction. Except in intense fields, where electric saturation may occur, it is proportional to the field strength, and we have $P_B = \alpha_B \cdot E$, where $\alpha_B = (D-1)/4\pi$, D being the

^{*} P. Gross and Schwarz, *Monatsch.*, 55, 287, 1930; P. Gross and Iser, *ibid.*, 55, 329, 1930.

[†] J. Physical Chem., 33, 1015, 1929.

[‡] Livens, Theory of Electricity, 2nd edition (1926), p. 82.

dielectric constant of the element of material, i.e. the molecule B. The work done in bringing the molecule to the distance r is thus

$$\int_0^E P_B \cdot \delta v_B \cdot dE = -rac{lpha_B e^2}{2D^2 r^4} \cdot \delta v_B$$
 .

Now when a molecule of the solute (B) is moved, an equal volume of the solvent (A) is displaced in the opposite direction and the work done in this process is similarly

$$+\alpha_A e^2 \cdot \delta v_B/2D^2r^4$$
,

so that the total work done in moving the given molecule A is

$$w = (\alpha_A - \alpha_B) \frac{e^2}{2D^2r^4} \cdot \delta v_B$$
.

If n_B° is the concentration of B at a great distance from the ion, its concentration at a distance r is therefore, by Boltzmann's theorem,

$$n_B = n_B{}^{\circ} e^{-\frac{\alpha_A - \alpha_B}{kT}} \cdot \frac{e^2}{2D^2r^4} \cdot \delta v_B$$

or to a first approximation, if the exponent is small,

$$n_B{}^{\circ} - n_B = n_B{}^{\circ} \left(\frac{\alpha_A - \alpha_B}{kT} \cdot \frac{e^2}{2D^2r^4} \cdot \delta v_B \right).$$

The total deficit in the amount of B round an ion, *i.e.* the amount salted out by a single ion, is obtained by integrating this over all the space round the ion. This is given by the integral

$$\int_{a}^{\infty} (n_{B}{}^{\circ} - n_{B}) \cdot 4\pi r^{2} \cdot dr = n_{B}{}^{\circ} \cdot \frac{\alpha_{A} - \alpha_{B}}{kT} \cdot \frac{4\pi \, \delta v_{B}}{2\,D^{2}} \cdot \frac{e^{2}}{a},$$

where a is the radius of the ion. If the solution contains c_1 gram ions of charge e_1 , c_2 gram ions of charge e_2 , etc., per litre, the number of molecules of B salted out per c.c. of solution is

$$\Gamma_B = n_B^{\circ} \cdot \frac{\alpha_A - \alpha_B}{kT} \cdot \frac{4\pi \, \delta v_B}{2 \, D^2} \cdot \sum \frac{e_1^{\ 2} c_1}{a_1} \cdot \frac{N_0}{1000} \cdot$$

Thus if the original solution contains n_B° molecules of B per c.c., its average effective concentration after the addition of the salt is $n_B^{\circ} + \Gamma_B$. Its activity coefficient will thus be increased by the salt in the ratio

$$f_B'/f_B = \frac{n_B^{\circ} + \Gamma_B}{n_B^{\circ}} = 1 + \frac{\Gamma_B}{n_B^{\circ}}.$$

If Γ_B/n_B° is small, we may make the approximation

$$\log (f_B'/f_B) = \Gamma_B/n_B^{\circ} = \frac{\alpha_A - \alpha_B}{kT} \cdot \frac{4\pi \,\delta v_B}{2D^2} \sum \frac{e_1^2 c_1}{a_1} \cdot \frac{N_0}{1000}.$$
(197)

This equation is equivalent to that of Debye and McAulay. $4\pi(\alpha_A - \alpha_B)$ is the difference between the dielectric constants of the substances A and B in the solution * and therefore $4\pi(\alpha_A - \alpha_B)\delta v_B$ is the dielectric constant lowering produced by a molecule of B in a c.c. of the solution. We thus have $D = D_0 - 4(\alpha_A - \alpha_B)\delta v_B$. n_B° , which permits the evaluation of this term.

It is evident that according to this equation the salting out is proportional to the dielectric constant lowering produced by the solute, and inversely proportional to the radius of the ions. Randall and Failey,† as a result of an examination of the available evidence, came to the conclusion that "there seems to be a qualitative agreement with these demands, but not a quantitative one". The available evidence, however, is neither very extensive nor exact.

*Salting out in Concentrated Solutions. The effect of salts on the partial free energies of non-electrolytes in concentrated solutions is more complicated. Thus although in dilute aqueous solutions the addition of a salt increases the partial vapour pressure of alcohol, in pure

* This statement is intended to give a concrete idea of the meaning of this term. It cannot be interpreted strictly since we cannot assign dielectric constants to the components of a solution.

+ Chem. Reviews, 4, 285, 1927, see also P. M. Gross, Chem. Reviews, 13, 91, 1933.

alcohol it must obviously cause a lowering. There must be a transition from the one kind of behaviour to the other. Figs. 24 and 25 show the effect of lithium chloride on the partial pressures of alcohol and water in solutions

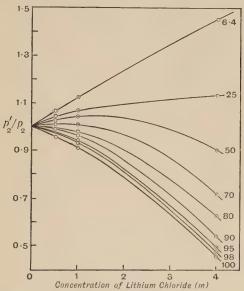


Fig. 24.—Effect of LiCl on partial pressures of water in water-alcohol solutions.

(Numbers on right are molar fractions of alcohol in the solvent.)

extending from pure water to pure alcohol.* Here p_1 , p_2 are the partial pressures of alcohol and water in solutions containing no lithium chloride, and p_1' , p_2' the corresponding values for a given concentration of the latter, and the ratios p_1'/p_1 and p_2'/p_2 are plotted against the concentration of lithium chloride (m). It can be seen

^{*} Shaw and Butler, Proc. Roy. Soc., A, 129, 519, 1930.

that while the partial pressure of water is increased by the salt in dilute solutions, it is decreased in concentrated solutions, and the partial pressure of water is decreased in the alcoholic solutions to a greater extent than in pure water.

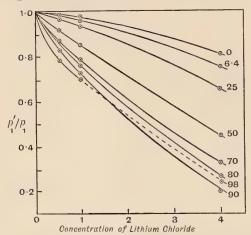


Fig. 25.—Effect of LiCl on partial pressures of water in water-alcohol solutions.

In order to understand this behaviour it is necessary to consider the thermodynamics of ternary solutions.* In the first place take a solution of a simple binary salt S_3 in a single solvent S_1 . If \bar{F}_3 , \bar{F}_1 are their partial free energies and n_3 , n_1 the number of mols of each present in the solution, we have by (118), at constant temperature and pressure

$$n_1 d\bar{F}_1 + n_3 d\bar{F}_3 = 0.$$
 (198)

If the salt concentration is very small,

$$ar{F}_3 = ar{F}_3^{\ \circ} + 2RT \log n_3$$
, or $n_3 \, dar{F}_3 = 2RT \cdot dn_3$,

^{*} Butler and Thomson, Proc. Roy. Soc., A, 141, 86, 1933.

so that we have

$$n_1 \left(\frac{d\bar{F}_1}{dn_3} \right) = -2RT$$
,

which is the usual ideal equation for the lowering of the partial free energy of the solvent by a binary salt.

Consider now a solution of n_3 mols of the salt in a mixed solvent containing n_1 mols of S_1 and n_2 mols of S_2 . By (118),

$$n_1 d\bar{F}_1 + n_2 d\bar{F}_2 + n_3 d\bar{F}_3 = 0.$$
(199)

If the concentration of the salt is very small we may write $n_3 d\bar{F}_3 = 2RT$. dn_3 as before, and we obtain

$$n_1 \left(\frac{d\bar{F}_1}{dn_3} \right) + n_2 \left(\frac{d\bar{F}_2}{dn_3} \right) = -2RT.$$
 (200)

Now if p_1' , p_2' , are the partial pressures of S_1 and S_2 in the ternary solutions, p_1 , p_2 their values in the corresponding binary solutions (i.e. same proportions of S_1 and S_2 , without S_3) and p_1° . p_2° their values for the pure liquids, we have

$$\begin{split} \bar{F}_1 = F^{\circ}_{1} + RT \log \; (p_1'/p_1^{0}) \; ; \\ \bar{F}_2 = F^{\circ}_{2} + RT \log \; (p_2'/p_2^{0}). \end{split}$$

Therefore (200) may be written as

$$n_1 \left(\frac{d \log_e(p_1'/p_1^{\circ})}{dn_3} \right) + n_2 \left(\frac{d \log_e(p_2'/p_2^{\circ})}{dn_3} \right) = -2.$$
 (201)

Applying (118) to the binary solutions of S_1 and S_2 , we obtain

$$n_1 \cdot d \log (p_1/p_1^{\circ}) + n_2 \cdot d \log (p_2/p_2^{\circ}) = 0,$$

and subtracting this from (201), we have

$$\begin{split} n_1 \left(\frac{d \log_{\mathbf{10}} \left({p_1}'/{p_1} \right)}{d n_3} \right) + n_2 \left(\frac{d \log_{\mathbf{10}} \left({p_2}'/{p_2} \right)}{d n_3} \right) \\ &= -\frac{2}{2 \cdot 303} = -0.87. \dots (202) \end{split}$$

This equation refers to very dilute solutions of the salt in which its activity coefficient can be taken as unity. It is, however, difficult to make sufficiently accurate measures of the effect of very small concentrations of a salt on the partial pressures of a mixed solvent. The following table shows the average values of the quantities on the left of (202) evaluated for the rather large interval of salt concentration from 0 to 1m. Notwithstanding that the equation $n_3 \cdot d\bar{F}_3 = 2RT \cdot dn_3$ is not exact to such a high concentration the sum of the two terms is approximately constant and reasonably near to the theoretical value.

TABLE XX.

CONFIRMATION OF (202) FOR WATER-ETHYL
ALCOHOL-LITHIUM CHLORIDE SOLUTIONS.

N_{2} ,	$n_2(d\log_{10}(p_2'/p_2)/dn_3).$	$n_1(d\log_{10}(p_1'/p_1)/dn_3)$.	Sum.
0	0.0	-0.75	-0.75
0.25	+0.26	-1.05	-0.79
0.50	+0.27	$-1 \cdot 12$	-0.85
0.70	+0.06	-0.91	-0.85
0.80	-0.11	-0.65	-0.76
0.90	-0.39	-0.34	-0.73
1.00	-0.72	0.0	-0.72

These equations give a relation between $d\bar{F}_1/dn_3$ and $d\bar{F}_2/dn_3$, but they do not tell us what are the individual values of these quantities. In order to distinguish when a component of a solution is salted out it is necessary to know what is the normal behaviour when there is no salting out. Dividing (200) by $(n_1 + n_2)$, we have

$$N_{1}(d\bar{F}_{1}/dn_{3})+N_{2}(d\bar{F}_{2}/dn_{3})=-2RT/(n_{1}+n_{2}),$$

where N_1 , N_2 are the molar fractions of S_1 (water) and S_2 (alcohol) in the solvent. If the salt S_3 has an equal

effect on the partial free energies of S_1 and S_2 , *i.e.* in the absence of salting out, we shall have

$$\frac{d\bar{F}_1}{dn_3} = \frac{d\bar{F}_2}{dn_3} = -\frac{2RT}{n_1 + n_2}, \quad \dots (203)$$

or in terms of the partial vapour pressures,

$$\frac{d \log (p_1'/p_1)}{d n_3} = \frac{d \log (p_2'/p_2)}{d n_3} = -\frac{2}{n_1 + n_2}. \dots (204)$$

These equations may be taken to represent the normal effect of a salt which interacts equally with both components of the solvent. When the effect of the salt on one component is greater (more positive) than this its effect on the other component is necessarily less (more negative). In Fig. 26 the curve AB shows the values of the quantities in (204) for the water-alcohol solutions. The actual values of $\Delta \log(p'/p)/\Delta n_3$, which are evaluated for the intervals 0 - 0.5m and 0 - 1.0m lithium chloride, are considerably displaced from this curve, the alcohol positively and the water negatively. The above calculation of the normal effect applies strictly only at very small salt concentrations, and a correction for the activity coefficient of the salt is necessary at greater concentrations. But the observed displacements are much greater than can be accounted for in this way, and it is necessary to conclude that the alcohol is salted out in the whole range of mixed solvents. The extent of the salting out, which is measured by the difference between the observed effect and the normal curve, decreases as the proportion of alcohol is increased.

The equations given above apply to extremely small salt concentrations for which its activity coefficient can be taken as unity. For solutions which are still sufficiently dilute for the application of the Debye-Hückel limiting law we may proceed as follows. The variation of the partial free energy of a binary salt may be expressed by

$$\overline{F}_3 = \overline{F}_3^{\circ} + 2RT \log m_3 - 2RT \cdot B'\sqrt{2m_3}$$

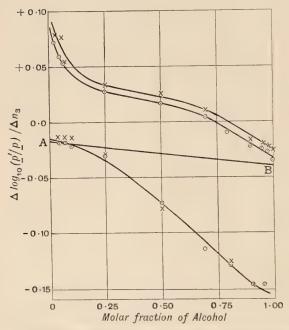


FIG. 26.—Effect of LiCl on the partial pressures of alcohol and water.

(Upper curves, alcohol; lower curve, water.)

$$-\bigcirc$$
 1 m . LiCl, $-\times$ - 0.5 m . LiCl.

and therefore

$$\left(\frac{d\overline{F}_3}{dm_3}\right) = \frac{2RT}{m_3} - 2RT B'(\sqrt{2}/2)m_3^{-\frac{1}{2}},$$

and since $m_3 = n_3 \cdot 1000/(n_1M_1 + n_2M_2)$, where M_1 and M_2 are the molecular weights of the two solvents, we have

$$n_3\!\left(\!\frac{d\overline{F}_3}{dm_3}\!\right)\!\!=\!\!\frac{n_1M_1+n_2M_2}{1000}(2RT-2RT\,.\,B'(\sqrt{2}/2)m_3^{\frac{1}{2}}).$$

Inserting this in (199), (200) is replaced by

$$\begin{split} n_1\!\left(\!\frac{d\overline{F}_1}{dm_3}\!\right) + & n_2\!\left(\!\frac{d\overline{F}_2}{dm_3}\!\right) \\ &= -\frac{n_1M_1 + n_2M_2}{1000} (2RT - 2RT \cdot B'(\sqrt{2}/2) m_3^{\frac{1}{2}}). \end{split}$$

We may thus take as the normal effect of the salt, when $d\overline{F}_1/dm_3 = d\overline{F}_2/dm_3,$

$$\frac{d\overline{F}_{1}}{dm_{3}} = \frac{d\overline{F}_{2}}{dm_{3}} = -\frac{n_{1}M_{1} + n_{2}M_{2}}{1000(n_{1} + n_{2})}\{2RT - 2RT, B'(\sqrt{2}/2)m_{3}^{\frac{1}{2}}\}.$$

Integrating the expression for \overline{F}_2 , we thus obtain in the absence of any salting out,

$$\overline{F}_2 \!=\! \overline{F}_2{}^{\circ} - \frac{n_1 M_1 + n_2 M_2}{1000 \left(n_1 + n_2\right)} \{ 2RTm_3 - 2RT \text{ , } B'(\sqrt{2}/3) m_3{}^{\frac{3}{2}} \},$$

or,
$$\bar{F}_2 = \bar{F}_2^{\circ} - \frac{n_3}{n_1 + n_2} \{ 2RT (1 - B'(\sqrt{2}/3) m_3^{\frac{1}{2}}) \}.$$

The proper measure of the salting-out in such solutions is thus the difference between the actual value of \overline{F}_2 and that given by this expression.*

* Cf. Matthews and Davies, J. Chem. Soc., p. 1435, 1933; also Osol and Kilpatrick, J. Amer. Chem. Soc., 55, 4430, 4440, 1933.

CHAPTER VIII

THE STANDARD FREE ENERGIES AND ENTROPIES OF IONS

Standard Free Energies of Ions in Aqueous Solutions. The partial molar free energy of an ion in solution is represented by:

 $\bar{F}_i = \bar{F}^{\circ}_{i} + RT \log \alpha_i,$

where a_i is the activity of the ion. For the solution of many problems concerning the equilibrium of solutions with other phases it is necessary to know the standard free energies \bar{F}° , as well as the activities of the ions. Since it is usually unnecessary to have absolute values of \bar{F}°_{i} , it is sufficient to take the free energies of the elements in a given state (in the case of gases at unit pressure) as zero. The value \bar{F}_{i}° depends on the way in which the activity is defined. As before, we shall suppose that the activity of an ion in any solvent becomes equal to its concentration (m) when the concentrations of the ion (and of other solutes) are very small. Since all methods of measuring partial free energies in solutions depend on the transfer from one phase to another of equivalent quantities of positive and negative ions, or the replacement of an ion by an equivalent quantity of ions of the same sign, it is only possible to determine directly either the sum of the values of \bar{F}°_{i} of equivalent quantities of ions of opposite sign, or the corresponding difference for equivalent quantities of ions of the same sign.

Determination from Standard Electrode Potentials. Consider the reversible cell:

$$H_2 \mid HCl(aq.) \mid Cl_2.$$
(a)

When positive electricity flows through the cell from left to right the reaction which takes place is

$$\frac{1}{2}H_2 + \frac{1}{2}Cl_2 = HCl(aq.).$$

If the sign of the electromotive force (E) is taken as that of the electrode on the right, $E\mathbf{F}$ is the electrical work yielded by this reaction, and this is equal to the free energy decrease, *i.e.* $E\mathbf{F} = -\Delta F$

Taking the free energy of the elements as zero, the free energy change in the reaction is

$$\Delta F = \bar{F}^{\circ}_{\mathbf{H}^{+}} + \bar{F}^{\circ}_{\mathbf{Cl}^{-}} + RT \log \alpha_{\mathbf{H}^{+}} \cdot \alpha_{\mathbf{Cl}^{-}},$$

and therefore

$$E\mathbf{F} = -(\bar{F}^{\circ}_{\mathbf{H}^{+}} - \bar{F}^{\circ}_{\mathbf{Cl}^{-}}) - RT \log a_{\mathbf{H}^{+}} \cdot a_{\mathbf{Cl}^{-}}.$$

Writing $E\mathbf{F} = E^{\circ}\mathbf{F} - RT \log \alpha_{\mathbf{H}^{+}} \cdot \alpha_{\mathbf{Cl}^{-}},$

where E° is the standard electromotive force of the cell, we see that $-E^{\circ}\mathbf{F} = \overline{F}^{\circ}_{H^{+}} + \overline{F}^{\circ}_{Cl^{-}}.$

The value of $\bar{F}^{\circ}_{\mathbf{H}^{+}} + \bar{F}^{\circ}_{\mathbf{Cl}^{-}}$ can thus be determined by measuring the electromotive force of the cell in a solution in which the activity of hydrogen chloride is known. It is not possible to determine the separate values of $\bar{F}^{\circ}_{\mathbf{H}^{+}}$ and $F^{\circ}_{\mathbf{Cl}^{-}}$ in this way, but no inconvenience arises in practice if we arbitrarily take \bar{F}° as zero for one particular ion. If we take $\bar{F}^{\circ}_{\mathbf{H}^{+}}$ as zero, we have

$$-E^{\circ}\mathbf{F} = \bar{F}^{\circ}_{\text{Cl}^{-}}.$$
(205)

Since E is the electromotive force of a chlorine electrode measured against a hydrogen electrode in the same solution, E° is the standard potential of the chlorine electrode measured against the standard hydrogen electrode. This quantity is taken as the standard electrode potential of chlorine for the given solvent. To obtain $\bar{F}^{\circ}_{\text{CI}^-}$ according to our conventions

$$(F_{\rm H_2} \! = \! 0, \ F_{\rm Cl_2} \! = \! 0, \ \bar{F}^{\circ}_{\rm H^+} \! = \! 0),$$

the standard electrode potential is multiplied by $-\mathbf{F}$, i.e.

$$\bar{F}^{\circ}_{\text{Cl}^-} = -E^{\circ}_{\text{Cl}_2} \mathbf{F} = -23074 E^{\circ}$$
 calories.

The standard free energies of positive ions can also be determined by means of suitable cells, and it is usually possible to devise cells without a liquid junction which will give the desired information. Since the chlorine electrode is not suitable for general use as a reference electrode, the calomel or similar electrode is usually employed as the electrode which is reversible with respect to the negative ion. Thus when a positive current passes from left to right through the cell

$$H_2 \mid HCl(aq.), HgCl(s) \mid Hg, \dots(b)$$

the reaction

$${\textstyle\frac{1}{2}}H_2 + HgCl(s) = H^+ + Cl^- + Hg$$

takes place, and therefore if E is the electromotive force, taking the sign as that of the electrode on the right, and ΔF the free energy change in this reaction,

$$E\mathbf{F} = -\Delta F$$
.

The free energy change in the reaction, taking $\bar{F}^{\circ}_{H^{+}}$, $F_{H_{2}}$, F_{Hg} as zero, is

$$\Delta F = \overline{F}^{\circ}_{\mathrm{Cl}^{-}} - F_{\mathrm{HgCl}(s)} + RT \log \alpha_{\mathrm{H}^{+}}$$
. $\alpha_{\mathrm{Cl}^{-}}$,

so that

$$E\mathbf{F} = -(\tilde{F}^{\circ}_{Cl^{-}} - F_{HgCl(s)}) - RT \log \alpha_{H^{+}} \cdot \alpha_{Cl^{-}}$$

Writing

$$E\mathbf{F} = E^{\circ}_{c}\mathbf{F} - RT \log \alpha_{\mathrm{H}^{+}} \cdot \alpha_{\mathrm{CI}^{-}},$$

where $E_e^{\,\circ}$ is the standard electromotive of the cell, it follows that

$$E_c^{\circ}F = -(F_{\text{Cl}}^{\circ} - F_{\text{HgCl}(s)}).$$
(206)

Consider now the cell

$$Hg \mid HgCl(s), LiCl \mid Li. \dots(c)$$

When a positive current passes through the cell from left to right the reaction is

$$Hg + Cl^- + Li^+ = HgCl + Li,$$

and the free energy in this reaction is

$$\Delta F = F_{\mathrm{HgCl}(s)} - \bar{F}^{\circ}_{\mathrm{Cl}^{-}} - \bar{F}^{\circ}_{\mathrm{Li}^{+}} - RT \log \alpha_{\mathrm{Cl}^{-}} \cdot \alpha_{\mathrm{Li}^{+}}.$$

If E is the electromotive force of the cell, taking the sign as that of the right-hand side, we thus have

$$E\mathbf{F} = -\Delta F$$
,

or $E\mathbf{F} = -F_{\mathrm{HgCl}(s)} + \bar{F}^{\circ}_{\mathrm{Cl}^{-}} + \bar{F}^{\circ}_{\mathrm{Li}^{+}} + RT \log \alpha_{\mathrm{Cl}^{-}} \cdot \alpha_{\mathrm{Li}^{+}},$ and if E° is the standard electromotive force of the cell defined by

 $E\mathbf{F} = E^{\circ}\mathbf{F} + RT \log \alpha_{\text{Cl}^{-}} \cdot \alpha_{\text{Li}^{+}},$

it is evident that

$$E^{\circ}\mathbf{F} = -F_{\mathrm{HgCl}(s)} + \overline{F}^{\circ}_{\mathrm{Cl}^{-}} + F^{\circ}_{\mathrm{Li}^{+}}.$$

Comparing with (206), it follows that

$$(E^{\circ} + E^{\circ}_{c})\mathbf{F} = \overline{F}^{\circ}_{\mathrm{Li}^{+}}.$$
(207)

 $(E^{\circ} + E^{\circ}_{c})$ is the standard electromotive force of the combination

$$H_2|HCl(aq.)|HgCl(s)|Hg-Hg|HgC.(s)LiCl(aq.)|Li, (d)$$

which is the same as that of the cell

$$H_2 \mid H^+ : Li^+ \mid Li$$

when any liquid-liquid junction potential is eliminated.

 $(E^{\circ} + E^{\circ}_{c}) = E^{\circ}_{Li^{+}}$ is thus the standard potential of the lithium electrode measured against the standard hydrogen electrode, and we have

$$E^{\circ}_{\mathrm{Li}^{+}}\mathbf{F} = \overline{F}^{\circ}_{\mathrm{Li}^{+}}.$$
 (208)

We can derive this relation directly from cell (d). The reaction which occurs in this cell when a positive current passes from left to right is

$$\frac{1}{2}H_2 + Li^+ + Cl^- = Li + H^+ + Cl^-$$

and the standard free energy change in this reaction is

$$\Delta F^{\circ} = F_{\mathrm{Li}} + \bar{F}^{\circ}_{\mathrm{H}^{+}} + \bar{F}^{\circ}_{\mathrm{Cl}^{-}} - (\frac{1}{2}F_{\mathrm{H}_{2}} - \bar{F}^{\circ}_{\mathrm{Li}^{+}} - \bar{F}^{\circ}_{\mathrm{Cl}^{-}}),$$

or, taking $F_{\rm H_2}$, $F_{\rm Li}$ and $\bar{F}^{\circ}_{\rm H^+}$ as zero.

$$\Delta F^{\circ} = -\bar{F}^{\circ}_{\mathrm{Li}^{+}}$$
.

Since $E^{\circ}_{\mathrm{Li}^{+}}\mathbf{F} = -\Delta F^{\circ}$, we have as before

$$E^{\circ}_{\mathbf{L}\mathbf{i}^{+}}\mathbf{F} = \bar{F}^{\circ}_{\mathbf{L}\mathbf{i}^{+}}.$$

In general, the standard free energy of a positive elementary ion M^{+z} is really the standard free energy change of the reaction,

$${
m M}+z{
m H}^{+}({
m aq.})={
m M}^{+z}({
m aq.})+z/2{
m H_{2}}$$
 ;

and is measured by $zE_{\text{M}}{}^{\circ}\mathbf{F} = \bar{F}{}^{\circ}{}_{\text{M}^{+}\text{Z}}$. The standard free energy of a negative elementary ion X is the standard free energy change of the reaction,

$$\frac{1}{2}H_2 + X = zH^+ + X^{-z},$$

and is measured by $-zE_X^{\circ}\mathbf{F} = \bar{F}_{X}^{\circ}-z$. Values of the standard free energies of the elementary ions are given in Table XXI (p. 186).

Standard Free Energy of Hydroxyl Ion. By (191)

$$\tilde{F}^{\circ}_{\mathrm{OH}^{-}} + \tilde{F}^{\circ}_{\mathrm{H}^{+}} = \tilde{F}^{\circ}_{\mathrm{W}} + RT \log K_{\mathrm{W}}.$$

Taking $\bar{F}^{\circ}_{H^+}$ as zero, we can thus find $\bar{F}^{\circ}_{OH^-}$ if we know \bar{F}°_{W} , which is equal to the free energy of formation from its elements of pure liquid water, and its dissociation constant K_{W} .

The former may be determined (p. 34) from the equilibrium constant of the gaseous reaction, combined with the free energy of vaporisation of water. We thus obtained

$$H_2 + \frac{1}{2}O_2 = H_2O$$
 (1), $\Delta F^{\circ}_{298} = -56640$.

It can also be determined indirectly from the free energy changes of such reactions as

(a)
$$Hg(1) + \frac{1}{2}O_2 = HgO$$
,

(b)
$$H_2 + HgO = Hg + H_2O$$
 (1).

The free energy change in reaction (a) can be determined by measurements of the dissociation pressure of mercuric oxide. In this way it has been found that

$$\Delta F^{\circ}_{298} = -13786$$
 cals.

The free energy change of reaction (b) can be determined from the electromotive force of the cell

Except for small differences due to the effect of the potassium hydroxide on the activity of water, the electromotive force of this cell is independent of the concentration of the solution. Brönsted found that the electromotive force, corrected to unit activity of water, was $E^{\circ} = 0.9268$ at 25°, corresponding to the free energy change for reaction (b), $\Delta F^{\circ}_{298} - zE^{\circ}\mathbf{F} = -42752$ calories. Adding together the free energy changes in reactions (a) and (b), we find

$$H_2 + \frac{1}{2}O_2 = H_2O(1), \ \Delta F^{\circ} = -56540.$$

Lewis and Randall give as the means of several independent methods of determination, $\Delta F = F^{\epsilon} w = -56560$.

Using this value and $K_{\rm W} = 1.008 \times 10^{-14}$, we obtain

$$\overline{F}^{\circ}_{OH^{-}} = -56560 - (-19110) = -37440$$
 calories.

Determination from Standard Oxidation Potentials.

When a positive current passes from left to right through the cell

H₂ | H⁺, Fe⁺⁺, Fe⁺⁺⁺ | Pt

the reaction is $\frac{1}{2}H_2 + Fe^{+} + = H^+ + Fe^{+} +$, and if E is the electromotive force, taken with the sign of the right-hand side, $E\mathbf{F} = -\Delta F$, where $-\Delta F$ is the free energy decrease in the reaction. Thus if E° is the standard potential of the ferrous-ferric electrode, referred to the standard hydrogen potential, $E^{\circ}\mathbf{F} = -\Delta F^{\circ}$, where

$$\Delta F^{\circ} = \bar{F}^{\circ}_{H^{+}} + \bar{F}^{\circ}_{Fe^{+}} - \bar{F}^{\circ}_{Fe^{+}} - \frac{1}{2} F_{H_{\circ}}.$$

Taking $F_{\mathbf{H}_2}$ and $\bar{F}^{\circ}_{\mathbf{H}^+}$ as zero, we thus have

$$E^{\circ}\mathbf{F} = \bar{F}^{\circ}_{\mathrm{Fe}^{+++}} - \bar{F}^{\circ}_{\mathrm{Fe}^{++}}$$
(209)

Taking $E^{\circ} = 0.748, * E^{\circ} \mathbf{F} = 17260$ cals., and

$$\bar{F}^{\circ}_{\text{Fe}^{++}} = -20240 \text{ cals.},$$

we find that $\bar{F}^{\circ}_{\text{Fe}^{+++}} = -2980 \text{ cals.}$

Another example is the determination of the standard free energy of the bromate ion from the potential of the bromine-bromic acid electrode.

In the cell

$$H_2 \mid H^+ \ \vdots \ HBrO_3, \ Br_2(1) \mid Pt$$

when a positive current passes from left to right, the reaction is

$$\frac{5}{2}H_2 + H^+ + BrO_3^- = \frac{1}{2}Br_2(l) + 3H_2O_3$$

and the standard free energy change is

$$\Delta F^{\circ} = 3 F_{\text{H}_{\circ}\text{O}} - \bar{F}^{\circ}_{\text{BrO}_{\circ}^{-}}.....(210)$$

^{*} Popoff and Kimz, J. Amer. Chem. Soc., 51, 382, 1929.

If E° is the standard electromotive force, $zE^{\circ}\mathbf{F} = -\Delta F$, where z, the number of equivalents in the reaction, is in this case 5. According to the measurements of Sammet, the value of E°_{291} , when the liquid junction potential is subtracted, is +1.491.*

Then
$$\Delta F^{\circ} = -5 \times 1.491 \times 23074 = -172000$$
 cals., and $\bar{b}^{\circ}_{\text{BrO}_3} = 172000 - 3 \times 56560 = 2300$ cals.

This quantity represents the standard free energy change in the reaction

$$\label{eq:Br2} \begin{array}{l} \frac{1}{2} Br_2(1) + \frac{1}{2} H_2 + \frac{3}{2} O_2 = H^+ + Br O_3^-. \end{array}$$

Determination from Equilibrium in Solution. Noves and Braun † determined the equilibrium reached when silver reacts with ferric nitrate solution to form ferrous nitrate and silver nitrate, according to the reaction:

$$Ag + Fe^{+++} = Ag^{+} + Fe^{++}$$
.

If $\bar{F}_{\text{Fe}^{+++}}$, \bar{F}_{Ag} , $\bar{F}_{\text{Fe}^{++}}$ are the partial free energies of the ions in the equilibrium solution, the condition of equilibrium is

$$F_{
m Ag} + ar{F}_{
m Fe^{+++}} = ar{F}_{
m Ag^{+}} + ar{F}_{
m Fe^{++}}.$$
 Writing $ar{F}_{
m Fe^{+++}} = ar{F}^{\circ}_{
m Fe^{+++}} + RT \log lpha_{
m Fe^{+++}},$ $ar{F}_{
m Fe^{++}} = ar{F}^{\circ}_{
m Fe^{++}} + RT \log lpha_{
m Fe^{++}},$ $ar{F}_{
m Ag^{+}} = ar{F}^{\circ}_{
m Ag^{+}} + RT \log lpha_{
m Ag^{+}},$

we have

$$\begin{split} F_{\mathrm{Ag}} + \overline{F}^{\circ}_{\mathrm{Fe}^{\uparrow++}} : - \overline{F}^{\circ}_{\mathrm{Fe}^{\downarrow+}} - \overline{F}^{\circ}_{\mathrm{Ag}^{\uparrow}} = & RT \log \left(\frac{\alpha_{\mathrm{Fe}^{\uparrow++}} \cdot \alpha_{\mathrm{Ag}^{+}}}{\alpha_{\mathrm{Fe}^{+++}}} \right) \\ = & RT \log K_{0}. \end{split}$$

Noyes and Braun determined the concentration ratios

$$K = m_{
m Fe^{++}}$$
 . $m_{
m Ag^{+}}/m_{
m Fe^{+++}}$

^{*} Calculated by Lewis and Randall, Thermodynamics, p. 521. † J. Amer. Chem. Soc., 34, 1016, 1912.

and plotting them against the total concentration they obtained by extrapolation to infinite dilution $K_0 = 0.128$.

Therefore $RT \log K_0 = -1218$. Putting $F_{\rm Ag} = 0, \ \ {\rm and} \ \ \bar{F}^{\circ}_{\rm Fe^{++}} = -20240, \ \ \bar{F}^{\circ}_{\rm Ag^{+}} = 18450,$

we thus obtain $\bar{F}^{\circ}_{\mathrm{Fe}^{+++}} = -3008.$

Determination from Solubility and Other Measurements. If F_s is the free energy of a solid salt which gives in solution ν_1 positive and ν_2 negative ions, and $(a \pm)_s$ its mean activity in the saturated solution, since the partial free energy in the saturated solution must be equal to F_s , we have

 $F_s = v_1 \bar{F}^{\circ}_{+} + v_2 \bar{F}^{\circ}_{-} + (v_1 + v_2) RT \log (\alpha \pm)_s. \dots (211)$

If F_s and $(a\pm)_s$ are known, the sum of the standard free energies of the ions in solution can be determined. Alternatively, if we know \bar{F}_+° and \bar{F}_-° and $(a\pm)_s$ we can find the free energy of the solid salt.

Example. In a saturated solution of sodium chloride at 25° ,

 $m=6\cdot 12$ and $f_{\pm}=1\cdot 013$; $\bar{F}^{\circ}{}_{\mathrm{Na^{+}}}=-62588$, $\bar{F}^{\circ}{}_{\mathrm{Cl^{-}}}=-31367$; therefore:

 $F_s = -62588 - 31367 + 2RT \log_e(6.12 \times 1.013) = -91792 \text{ cals.}$

This is the free energy change in the formation of solid sodium chloride from sodium and chlorine at unit pressure at 25°. *i.e.*

$$Na + \frac{1}{2}Cl_2(g) = NaCl(s)$$
; $\Delta F^{\circ}_{298\cdot 1} = -91792$ cals.

The determination of the standard free energy of the ammonium ion in solution may be given as a case in which the solubility of a gas is used as one step in the calculation. The free energy of formation of gaseous ammonia, as determined from the study of the gas reaction (p. 36) is

$$\frac{1}{2}N_2 + 3/2H_2 = NH_3(g)$$
; $\Delta F^{\circ}_{298} = -3910$ cals.,

i.e. the free energy of gaseous ammonia at unit pressure at 25°, taking the free energies of the elements as zero, is $F^{\circ}(\mathbf{g}) = -3910$ cals. Its free energy at a pressure p (atmos.) is $F(\mathbf{g}) = F^{\circ}(\mathbf{g}) + RT \log p$. Similarly, if $\bar{F}^{\circ}_{\mathrm{NH}_3}$ is the standard free energy in aqueous solution, its partial free energy in a dilute solution of concentration m is $\bar{F}^{\circ}_{\mathrm{NH}_3} + RT \log m$, and the condition of equilibrium between the gas and the solution is

$$F^{\circ}(\mathrm{g}) + RT \log \, p = ar{F}^{\circ}{}_{\mathrm{NH_3}} + RT \log \, m, \ ar{F}^{\circ}{}_{\mathrm{NH_3}} - F^{\circ}(\mathrm{g}) = - \, RT \log (m/p).$$

or

and therefore

It has been found * that the limiting value of (m/p) at small concentrations is $(m/p)_0 = 59.2$. Using this value, we find that

$$\begin{split} \bar{F}^{\circ}{}_{\rm NH_3} - F^{\circ}({\rm g}) &= -2420 \ {\rm cals.}, \\ \bar{F}^{\circ}{}_{\rm NH_3} &= -6330 \ {\rm cals.}. \end{split}$$

The standard free energy of $\mathrm{NH_4OH}$ is obtained by adding the free energy of water in the solution to $\bar{F}^{\circ}_{\mathrm{NH_3}}$, *i.e.*

$$\begin{split} \bar{F}^{\circ}{}_{\mathrm{NH_4OH}} &= \bar{F}^{\circ}{}_{\mathrm{NH_3}} + \bar{F}_{\mathrm{H_2O}} \\ &= -6330 - 56560 = -62890 \text{ cals.} \end{split}$$

Finally, if K is the dissociation constant of ammonium hydroxide, we have (p. 155),

$$ar{F}^{\circ}_{\mathrm{NH_4OH}} - ar{F}^{\circ}_{\mathrm{NH_4^+}} - F^{\circ}_{\mathrm{OH}^-} = RT \log K.$$
 Taking $ar{F}^{\circ}_{\mathrm{OH}^-}$ as -37440 and K as $1\cdot79\times10^{-5}$, i.e. $(RT\log_e K = -6480 \text{ cals.}),$ we have $ar{F}^{\circ}_{\mathrm{NH_4^+}} = -18970 \text{ cals.}$

* de Wijs, Rec. Trav. Chem., 44, 655, 1925.

This quantity actually represents the standard free energy change in the reaction

$$1/2N_2 + 3/2H_2 + H^+(aq.) = NH_4^+(aq.).$$

TABLE XXI.

Standard Free Energies of Ions relative to $\overline{F}^{\circ}_{\mathrm{H}^{+}}\!=\!0$ in Aqueous Solution at $25^{\circ}.$

Cl-	-34345	Ag^{+}	18448	Fe^{++}	-20240
Br^-	-24574	Tl^+	-7760	Fe^{+++}	-2990
I-	-12333	Cu^{++}	15912	ClO_3	-250
Li^+	+68248	Zn^{++}	-34984	${ m BrO_3}^-$	2300
Na^{+}	-62588	Cd^{++}	-18348	10^{3}	-31580
\mathbf{K}^{+}	-67431	Pb^{++}	-5551	$^{ m OH-}$	-37440
Rb^+	-67473	$\mathrm{Hg_2}^{++}$	36854		
$\mathrm{NH_4^+}$	-18930	Sn^{++}	-6276		

Standard Entropies of Ions in Aqueous Solutions. If \bar{F} and \bar{H} are the partial free energies of a salt in a solution, the partial entropy is

 $\bar{S} = \frac{\bar{H} - \bar{F}}{T}$.

In very dilute solutions $\bar{F} = \bar{F}^{\circ} + (\nu_1 + \nu_2) RT \log m_{\pm}$, and \bar{H} is equal to the partial heat content for an infinitely dilute solution \bar{H}° , so that

$$\bar{S} = \frac{\bar{H}^{\circ} - \bar{F}^{\circ}}{T} - (\nu_1 + \nu_2) R \log m_{\pm}. \quad \dots (212)$$

The quantity $\frac{\bar{H}^{\circ} - \bar{F}^{\circ}}{T} = \bar{S}^{\circ}$ is called the standard entropy of the salt. It can be readily determined when \bar{H}° and \bar{F}° are known.

The absolute values of the standard entropies of a considerable number of salts have been calculated by Latimer and Buffington.* In the previous sections we evaluated the standard free energies of salts in aqueous solution at 25°, taking the free energies of the elements as zero at this temperature. The value of \bar{H}° can easily be determined with reference to the same standard (i.e. \bar{H}° is then the heat content change in the formation of a mol of the salt at infinite dilution from the elements).

We thus obtain by $(\bar{H}^{\circ} - \bar{F}^{\circ})/T$ the standard entropy relative to the entropies of the elements. If we add the entropies of the elements at the given temperature, we obtain the absolute standard entropy of the salt in the solution. Some examples of this calculation are given in Table XXII.

TABLE XXII.

		\overline{H}° . Heat Content at $m=0$, relative to Elements.	F°. Standard Free Energy relative to Elements.	$(H^{\circ}-F^{\circ})/T$. Standard Entropy relative to Elements.	Entropy of Elements at 25° C.	(Alsolute).
CuCl ₂	-	-62.6*	-46.9*	- 52	8 + 51	7
CuBr ₂	-	-40.6	-33.2	-25	8 + 36	19
FeCl ₃	-	-127.7	- 96.8	-104	7 + 76	-21
$FeBr_{s}$	-	-95.5	-76.0	- 65	7 + 55	- 3
$TlBr_3$	-	-56.4	-27.3	-98	18 + 55	-25

* In kgm. cals.

It is often convenient to start with the entropy of the solid salt and to determine the entropy of solution. Since the free energy of the solid salt (\bar{F}_s) is equal to its partial free energy in a saturated solution, we have

$$\bar{F}_{\circ} = \bar{F}^{\circ} + RT \log \alpha_{\circ}$$

where a_s is the activity in the saturated solution. We can thus evaluate $\Delta F^{\circ} = \bar{F}^{\circ} - F_s$, when the activity of the

^{*} J. Amer. Chem. Soc., 48, 2297, 1926.

salt in the saturated solution is known. Similarly, the heat of solution of the salt in an infinitely dilute solution gives $\Delta H^{\circ} = \vec{H}^{\circ} - H_s$.

 $\Delta S^{\circ} = (\Delta H^{\circ} - \Delta F^{\circ})/T$, which may be called the entropy of solution, is thus the difference between the standard entropy in the solution and the entropy of the solid salt. If we add the value of the latter we obtain the absolute value of \tilde{S}° . The details of this calculation for a number of salts are given in Table XXIII.

TABLE XXIII.

Standard Entropies of Salts Determined from the Entropy of the Solid Salt and the Entropy of Solution at 25° .

		Entropy of Substance.	ΔH° . kgm. cals.	ΔF° , kgm. cals.	ΔS° .	\overline{S}° (Absolute).
HCl	-	+44.5	-17.3	-8.7	-28.9	+15.6
$_{ m HBr}$	- `	47.0	-19.9	-12.0	$-26 \cdot 4$	20.6
HI	-	49.0	-19.2	-12.7	-21.9	$27 \cdot 1$
NaCl	-	18.5	+1.0	$-2\cdot2$	+10.6	29.1
KCl	-	19.7	4.4	-0.9	18.0	37.7
AgCl	-	24.0	16.0	+13.3	9.0	33.0
AgBr	-	25.0	20.1	16.6	11.8	36.8
AgI	-	26.8	26.4	21.8	15.6	42.4
MgF_2	-	15.7	-2.8	10.7	-45.0	-29.3
CaF ₂		17.2	+2.7	13.9	-37.3	-20.1
PbF ₂	-	22.0	+2.2	10.1	-26.3	-4.3
BaSO ₄	-	38.0	5.6	13.1	-25.0	13.0

Finally, the difference between the standard entropies of two ions may be obtained from the consideration of replacement reactions. The standard entropy change in the reaction $Na + H^+ = Na^+ + \frac{1}{2}H_2$ is given by

$$\Delta S^{\circ} = (\Delta \mathbf{H}^{\circ} - \Delta F^{\circ})/T,$$

where ΔH° is the heat of solution (at infinite dilution) in very dilute solutions of hydrogen ions, and ΔF° is obtained in calories by multiplying the standard electrode potential of sodium, referred to the standard hydrogen electrode by 23,074. Since

$$\Delta S^{\circ} = \overline{S}^{\circ}_{\mathbf{N}\mathbf{a}^{+}} + \frac{1}{2}S_{\mathbf{H}_{2}} - S_{\mathbf{N}\mathbf{a}} - \overline{S}^{\circ}_{\mathbf{H}^{+}},$$

we obtain the absolute value of $\bar{S}^{\circ}_{Na^{+}} - \bar{S}^{\circ}_{H^{+}}$ by adding to ΔS° the absolute value of $S_{Na} - \frac{1}{2}S_{H_{2}}$ (Table XXIV.).

TABLE XXIV. Entropy Changes in Replacement of $\mathrm{H^{+}}$ by other Ions at 25° .

Ion.		ΔH° , kgm. cals.	ΔF° , kgm. cals.	ΔS°	Entropy of Element.	S Mo12-250 HF.
ξH,	_				14.7	
Ľi "	-	-66.0	- 68.3	7.7	7.6	0.5
Na	-	-56.8	-62.6	19.3	12.3	16.8
K	-	-61.5	-67.4	19.9	16.6	21.8
Rb	-	-60.8	-67.5	$22 \cdot 4$	17.4	25.8
Cu	-	-129.0	- 131.9	9.7	10.6	~ 9-1
Zn		-36.3	-35.0	-4.3	9.8	-23.9
Cd	_	-17.1	-18.3	4.0	11.8	-13.6
Fe	-	-20.7	-20.3	-0.1	7.7	-21.8
Sn	-	- 4.5	6.3	6.0	11.2	$-12\cdot2$

It is not possible to determine the standard entropies of individual ions from these values. It is sufficient, however, for thermodynamical calculations to know relative values, taking that of one particular ion as zero. In finding the relative standard free energies we adopted the convention that $\bar{F}^{\circ}_{H^{+}}=0$. Similarly the relative standard entropies of the ions are determined taking $\bar{S}^{\circ}_{H^{+}}=0$. The values of these quantities so far determined are given in Table XXV.

TABLE XXV.

Standard Entropies of Ions in Aqueous Solution at 25° relative to $\overline{S}^\circ_{\text{H}^+}{=}0$ (calories/deg.).*

Li^+	1	Ag^+	18.3	Fe^{++}	-22
Na^+	15	TI^+	28.6	Fe^{+++}	- 67
K^{+}	21.5	Mg^{++}	-19	Pb^{++}	2
Rb^{+}	25	Ca++	-11.4	TI^{+++}	-87
\mathbf{F}^{-}	-5	Ba ⁺⁺	0.8	CO_3 =	-14
Cl-	$15 \cdot 6$	Zn^{++}	-24	OH-	-2
Br^-	20.5	Cu++	-23	NO_3^-	-36.9
I-	27	Cd^{++}	-14	ClO ₄ -	46.2
				$C_2O_4^=$	9.3

Applications. (1) Calculation of standard potential of the fluorine electrode. The heat of formation of sodium fluoride in aqueous solution at infinite dilution, from the elements, is

$$Na + \frac{1}{2}F_2 = Na^+(aq.) + F^-(aq.)$$
;
 $\Delta H^{\circ}_{298} = -136000$ calories.

Taking the entropy of Na as $12\cdot3$ and of $\frac{1}{2}F_2$ as $23\cdot5$, and the standard entropies of the ions as given in Table XXV., we have

$$\Delta \bar{S}^{\circ} = \bar{S}^{\circ}_{Na^{+}} + \bar{S}^{\circ}_{F^{-}} - S_{Na} - \frac{1}{2}S_{F_{2}} = -25.8,$$

and therefore the standard free energy change is

$$\Delta \bar{F}^{\circ} = \Delta H^{\circ} - T \Delta S^{\circ} = -128{,}300$$
 calories.

Taking the free energies of the elements as zero, we have

$$\Delta F^{\circ} = \bar{F}^{\circ}{}_{\mathrm{Na^{+}}} + \bar{F}^{\circ}{}_{\mathrm{F^{-}}}.$$

Since
$$\bar{F}^{\circ}_{Na^{+}} = -62,600$$
, we have $\bar{F}^{\circ}_{F^{-}} = -65,700$.

* Bibliography of papers by Latimer and colleagues: J. Amer. Chem. Soc., 48, 2297, 2868, 1926; 50, 2202, 3286, 1928; 51, 2293, 1929; 52, 549, 1930; 54, 1900, 1932; 55, 1971, 1933; Z. phys. Chem., A, 148, 464, 1930; J. Chem. Physics, 1, 424, 620, 1933.

The standard potential of the fluorine electrode is thus

$$E^{\circ} = -\frac{\bar{F}^{\circ}_{F^{-}}}{F} = +2.85 \text{ volts.}$$

(2) Standard potential of the magnesium electrode. The heat content change in the reaction

$$Mg + 2H^{+} = Mg^{++} + H_{2}$$

as determined by the heat of solution of magnesium in dilute hydrochloric acid is $\Delta H^{\circ}_{298} = -110200$ cals. The standard entropy change is

$$\Delta S^{\circ} = \overline{S}^{\circ}_{\mathbf{Mg}^{++}} + S_{\mathbf{H}_{2}} - S_{\mathbf{Mg}} - 2\overline{S}^{\circ}_{\mathbf{H}^{+}}.$$

Taking $\bar{S}^{\circ}_{Mg^{++}} = -19$, $S_{H_2} = 29.4$, $S_{Mg} = 8.3$, and $\bar{S}^{\circ}_{H^+} = 0$, we have $\Delta S_0 = 2.1$ and $\Delta F^{\circ} = -110,800$ cals. Since $2E^{\circ}\mathbf{F} = \Delta F^{\circ}$, where E° is the standard potential of the magnesium electrode, we have $E^{\circ} = -2.40$ volts.

Latimer has calculated the free energies of the ions and the electrode potentials of beryllium, magnesium, calcium, strontium, and barium in this way,* with the following results.

$$\label{eq:table_XXVI} \begin{split} \text{Reaction}: \ \mathbf{M} + 2\mathbf{H}^+ = \mathbf{M}^{++} + \mathbf{H_2}. \end{split}$$

	Meta	1.	$\Delta F^{\circ}.$	E° .
Ве	_	-	-77900	-1.69
Mg	-	-	-110800	-2.40
Ca	-	-	-132700	-2.87
Sr	_	-	-134700	-2.92
Ba	-	-	-134000	-2.90

* J. phys. Chem., 31, 1267, 1927. The entropies of the beryllium and strontium ions were estimated from the empirical relation between entropy of solution and the ionic radius which is given later.

(3) Standard potential of the aluminium electrode. Direct measurements of this potential have given extremely discordant values. It may be calculated from the free energy change in the reaction

$$Al + 3H^{+} = Al^{+++} + 3/2H_{2}$$
.

This can be determined if the heat of the reaction and the standard entropy of Al⁺⁺⁺ are known. The latter could be determined as in Table XXIII. from the entropy and entropy of solution of a suitable salt, but none of the simple salts of aluminium are suitable for the purpose. Latimer and Greensfelder * therefore used the caesium alum CsAl(SO₄)₂. 12H₂O. They determined the entropy of the solid salt by heat capacity measurements, finding $S_{298\cdot 1} = 163\cdot 85$. The heat of solution of the salt in water at 25° is $\Delta H^{\circ} = \overline{H}^{\circ} - H_s = 13560$ calories. The free energy of solution $\Delta F^{\circ} = \overline{F}^{\circ} - F_s = -RT \log \alpha_s$ can be determined when the concentration in the saturated solution and the activity coefficient are known. It was found that the concentration of the saturated solution at 25° was m = 0.01403, and $f_{\pm} = 0.217$. Hence $\bar{F}^{\circ} - F_{s} = +12910$ calories. The entropy of solution is thus $\Delta S^{\circ}_{\text{soln.}} = \bar{S}^{\circ} - \bar{S}_{s} = (\Delta H^{\circ} - \Delta F^{\circ})/T = +2.18$, and the absolute value of $S_{\text{soln.}}^{\circ} = 163.85 + 2.18 = 166.03$.

Since
$$\bar{S}^{\circ} = \bar{S}^{\circ}_{Cs^{+}} + \bar{S}^{\circ}_{Al^{+++}} + 2\bar{S}^{\circ}_{8O_{4}} = +12S_{H_{2}O},$$

taking $\bar{S}^{\circ}_{Cs^{+}}$ as $27\cdot9$, $\bar{S}^{\circ}_{8O_{4}}$ as 9 , $S_{H_{2}O}$ as $15\cdot9$, we find that $\bar{S}^{\circ}_{Al^{+++}} = -70\cdot9.$

The standard entropy change in the reaction

$${\rm Al} + 3{\rm H}^+ = {\rm Al}^{+++} + 3/2{\rm H}_2,$$
 taking $S_{\rm Al} = 6\cdot 8,\ 3/2S_{\rm H_2} = 43\cdot 8,\ \overline{8}^{\circ}_{\rm H^+} = 0,$ is thus $-33\cdot 9.$

* J. Amer. Chem. Soc., 50, 2202, 1928.

 ΔH° for the reaction, as given by the heat of solution of aluminium in dilute hydrochloric acid, is -127000 cals. Therefore the standard free energy change is

$$\Delta F^{\circ}_{298} = \Delta H^{\circ} - T\Delta S^{\circ} = -116900$$
 cals.

Writing $\Delta F^{\circ}_{298} = +3\mathbf{F}E^{\circ}$, we have for the standard electrode potential of aluminium $E^{\circ} = -1.69$ volts.

(4) Standard free energy of the sulphate ion. The entropy of solid barium sulphate (BaSO₄), as determined by heat capacity measurements, is $31\cdot 5$ at 25° C. Its heat of solution in water is $\Delta H^{\circ}_{298} = 5455$ cals. The free energy of solution is $\Delta F^{\circ} = F_0 - \tilde{F}_s = -2RT \log(mf_{\pm})$. Taking the solubility as $m = 0.957 \times 10^{-5}$ and $f_{\pm} = 0.997$, we obtain $\Delta F^{\circ} = 13718$ cals. The entropy of solution $\Delta S^{\circ} = (\Delta H^{\circ} - \Delta F^{\circ})/T$ is thus $\Delta S^{\circ} = -27\cdot 7$, and combining this with the entropy of the solid, we have

$$\bar{S}^{\circ}_{Ba^{++}} + \bar{S}^{\circ}_{SO_4} = 31.5 - 27.7 = 3.8 \text{ cals./deg.}$$

The value of $\bar{S}^{\circ}_{Ba^{++}}$ (determined similarly to $\bar{S}^{\circ}_{Mg^{++}}$ in (2)) is 0·8, and therefore $\bar{S}^{\circ}_{SO_4} = 3\cdot0$. As a result of measurements of this kind with several sulphates, Latimer, Hicks and Schutz* gave $\bar{S}^{\circ}_{SO_4} = 3\cdot8$ as the best value.

The heat of formation of pure sulphuric acid from its elements is

$$S_{rh} + H_2 + 2O_2 = H_2SO_4(1), \quad \Delta H^{\circ}_{298\cdot 1} = -194,120,$$

and the heat of solution of $\mathrm{H_2SO_4}$ in water at infinite dilution is

$$H_2SO_4(1) = H_2SO_4(aq.), \quad \Delta H_{298\cdot 1}^{\circ} = -20900;$$

* Latimer, Hicks and Schutz, *J. Chem. Physics*, 1, 424, 622, 1933.

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The heat of formation of sulphuric acid in aqueous solution at infinite dilution is thus

$$S_{(rh)} + H_2 + 2O_2 = 2H^+ + SO_4^-, \quad \Delta H^{\circ}_{298\cdot 1} = -215000 \text{ cals.}$$

The entropy change in this reaction, taking the following values for the entropy, $H_2 = 31 \cdot 23$, $S = 7 \cdot 6$, $O_2 = 49 \cdot 03$, $SO_4 = 3 \cdot 8$, is $\Delta S^{\circ} = -133$.

The free energy change in the reaction,

$$\Delta F^{\circ} = \Delta H^{\circ} - T \Delta S^{\circ},$$

is thus -175300 cals., which is equal to the free energy of formation of the sulphate ion $F^{\circ}_{SO_4}$ =, taking $F^{\circ}_{H^+}$ as zero.

Similar determinations have been made of the standard entropies and free energies of the nitrate, chlorate and oxalate ions, the results of which are given in Table XXVII.

TABLE XXVII.

*Entropy of Solution of Simple Gas Ions. The entropy of monatomic ions in the gaseous state can be calculated by means of Sackur's equation (p. 50),

$$S_{\text{gas}} = 25.7 + 3/2R \log \text{ (atomic wt.)}.$$

Subtracting the standard entropy of the ion in aqueous solution from this quantity, we obtain the entropy of solution of the gaseous ion. Some values are given in Table XXVIII. Since the standard entropies in solution are relative to $\bar{S}_{\rm H^+}{}^{\circ}=0$, the values of the entropy of solution differ from their absolute values by the absolute value of $z\bar{S}_{\rm H^+}{}^{\circ}$.

TABLE XXVIII.

ENTROPIES OF SOLUTION OF SIMPLE GAS IONS.

	Sg.	ΔS of Solution of Gas Ion.	,	S_g .	ΔS of Solution of Gas Ion.	,	S_g .	ΔS of Solution of Gas Ion.
Li ⁺ Ag ⁺ Na ⁺ Tl ⁺ K ⁺ Rb ⁺	31.5 $ 39.7 $ $ 35.1 $ $ 41.6 $ $ 36.6 $ $ 39.0$	31 24 20 15 15	F- Cl- Br- I- Zn++ Cu++	34·5 36·4 38·8 40·1 38·3 38·2	39 21 19 13 62 61	Fe ⁺⁺ Sn ⁺⁺ Mg ⁺⁺ Ca ⁺⁺ Ba ⁺⁺	37·7 39·9 35·2 36·7 40·4	59 52 53 46 36

Latimer and Buffington found that the entropy of solution varied inversely with the radius of the ion as determined by the crystal measurements of Bragg, and the values for uni- and bivalent positive ions are fairly closely represented by the equations:

$$\Delta S_{\mathrm{M}^+} = -12 \cdot 6 + 58 \cdot 6(1/r),$$

 $\Delta S_{\mathrm{M}^{++}} = -9 \cdot 5 + 94 \cdot 5(1/r).$

These equations can be used, in conjunction with the Sackur equation, to obtain an estimate of the entropy in solution of ions for which no direct determination is available.*

*Standard Free Energies of Ions in Other Solvents. Very little information is available as to the standard free energies of ions in single solvents other than water. The difference between the standard free energies of a slightly soluble salt in two solvents can be estimated from the solubilities. Since the partial free energy of a salt in a saturated solution is equal to the free energy of the solid

^{*} If the ionic radii of Goldschmidt are employed the agreement with this linear relation is not good.

or

salt, we have for a salt giving ν_1 positive and ν_2 negative ions:

$$F_{s} = \bar{F}^{\circ\prime} + (\nu_{1} + \nu_{2})RT \log \alpha'_{\pm},$$

$$F_{s} = \bar{F}^{\circ\prime\prime} + (\nu_{1} + \nu_{2})RT \log \alpha_{\pm}^{\prime\prime},$$

$$\bar{F}^{\circ\prime\prime} - \bar{F}^{\circ\prime} = (\nu_{1} + \nu_{2})RT \log \alpha_{+}^{\prime}/\alpha_{+}^{\prime\prime}, \dots (213)$$

where a_{\pm}' , a_{\pm}'' are the mean activities of the ions in saturated solutions in the two solvents, and $\bar{F}^{\circ\prime}$, $\bar{F}^{\circ\prime\prime}$ the standard free energies. The mean activity can be determined from the concentration, using the activity coefficient calculated by the Debye-Hückel expression, if the solubility is sufficiently low. a_{\pm}'/a_{\pm}'' is the corrected distribution ratio of the salt between the two solvents. Table XXIX shows the values of these quantities for some saturated solutions of perchlorates in water and methyl alcohol.*

TABLE XXIX.

ACTIVITIES OF PERCHLORATES IN SATURATED SOLUTIONS IN WATER AND METHYL ALCOHOL AT 20.

Cation.					a_{\pm} in Water.	$lpha_{\pm}$ in Methyl Alcohol.	$(\alpha_{\pm})_{\mathrm{W}}/(\alpha_{\pm})_{\mathrm{MeOH}}$.
K ⁺ Rb ⁺ Cs ⁺	-	-	-		0·111 0·057 0·0664	$0.00436 \\ 0.00203 \\ 0.00253$	28.0
[Co(N] (Co(N]	$H_3^-)_4^ H_3^-)_4^-$.	${ m NO_3)_2} \ { m NO_2}$. CSN	1)+	0.0247	$ \begin{array}{c} 0.00233 \\ 0.00143 \\ 0.00343 \end{array} $	17.3

The mean activity of the salt is related to the individual ion activities by $(a_{\pm})^{\nu_1+\nu_2} = a_1^{\nu_1}a_2^{\nu_2}$, so that

$$\left(\frac{\alpha_{\pm^{'}}}{\alpha_{\pm^{''}}}\right)^{\nu_1+\nu_2} = \frac{{\alpha_1}'^{\nu_1}{\alpha_2}'^{\nu_2}}{{\alpha_1}'^{'\nu_1}{\alpha_2}'^{'\nu_2}}. \dots (214)$$

^{*} Bronsted, Delbanco and Volqartz, Z.~phys.~Chem.,~A,~162,~128,~1932.

It is not, however, possible to determine the separate values of the ratios a_1'/a_1'' , etc., since in no operation which is practically possible can we transfer a single ion from one phase to another. It is therefore impossible to split $(\bar{F}^{\circ\prime} - \bar{F}^{\circ\prime\prime})$ into the values of the separate ions. Indeed it will be shown in the next section that these quantities have not a single definite value for two given

phases. However, if we arbitrarily give a'/a'' a definite value for one particular ion, it is possible to determine

the relative values of other ions by (214).

Taking the ratio of the activities of the chloride ion in water and methyl alcohol as $100 ((\alpha_{\rm Cl})_{\rm W}/(\alpha_{\rm Cl})_{\rm Me} = 100)$, Bronsted, Delbanco and Volqartz obtained the following values of the distribution ratios $\alpha_{\rm W}/\alpha_{\rm Me}$ for other ions.

TABLE XXX.

Relative Distribution Ratios of Ions between Water and Methyl Alcohol at 25° .

Cl⁻ Br⁻ I⁻ NO₃⁻ ClO₃⁻ BrO₃⁻ IO₃⁻ ClO₄⁻ $C_2H_3O_2$ ⁻ SO₄⁻ 100 39·1 5·3 28·8 45·2 354 2790 5·8 224 2160 K⁺ Rb⁺ C_5 ⁺ [Co(NH₃)₄(NO₂)₂]⁺ [Co(NH₃)₄, NO₂, CSN)]⁺ 122 143 131 4 8·3

According to the Debye-Hückel theory the difference between the standard free energy of a salt in two solvents is equal to the difference between the electrical work of charging the ions in these media. By the simple electrical theory the work of charging an ion of radius r in a medium of dielectric constant D is $e^2/2rD$, and the difference of the standard free energies for a gram molecule of salt in media having dielectric constants D' and D'' is therefore

$$\bar{F}^{\circ\prime} - \bar{F}^{\circ\prime\prime} = N_0 \sum \frac{\nu_1 e^2}{2r_1} \left(\frac{1}{D_1'} - \frac{1}{D^{\prime\prime}} \right), \dots (215)$$

where N_0 is the Avogadro number, and the summation extends over all the ions. Bjerrum * has suggested that a term should be added to this representing the free energy difference of similar neutral molecules in the two solvents, viz.,

$$\bar{F}^{\circ\prime} - \bar{F}^{\circ\prime\prime} = (\bar{F}^{\circ}{}_{n}{}^{\prime} - \bar{F}^{\circ}{}_{n}{}^{\prime\prime}) + N_{0} \sum \frac{v_{1}e_{1}{}^{2}}{2r_{1}} \bigg(\frac{1}{D^{\prime}} - \frac{1}{D^{\prime\prime}}\bigg).$$

In this equation the term $N_0 \sum \frac{\nu_1 e_1^2}{2r_1} \left(\frac{1}{D'} - \frac{1}{D''}\right)$ represents that part of the standard free energy which arises from the electrical charges on the ions and $(\bar{F}^{\circ}{}_{n}{}' - \bar{F}^{\circ}{}_{n}{}'')$ that which arises from interactions of other kinds between the ions and the solvents. Thus for potassium and chloride ions $\bar{F}^{\circ}{}_{n}{}' - F^{\circ}{}_{n}{}''$ will be taken as the standard free energy difference of the similar uncharged atoms of argon in the two solvents. This is equal to $RT \log a''/a'$, where a''/a' is the distribution ratio of argon between the two solvents. It appears to be possible to account approximately for the solubilities of salts in this way.

It is necessary to point out that the expression $e^2/2rD$ is probably only a very rough approximation to the work of charging ions in actual media. Webb† has made a careful calculation of this quantity, taking into account the electric saturation due to dipole orientation near the ions, and has obtained values which differ widely from the simple expression.

A number of investigations have been made of the variation of the standard free energies of salts in aqueous solutions produced by the addition of non-electrolytes

^{*} Bjerrum and Larrson, Z. phys. Chem., A, 127, 358, 1927; Bjerrum and Josefovicz, ibid., A, 159, 194, 1932.

[†] J. Amer. Chem. Soc., 48, 2589, 1926.

which lower the dielectric constant of the solution. According to (215) the difference between the standard free energy in water (D_0) and in a solution of dielectric constant D is given by $\Delta \bar{F}^\circ = -N_0 \sum_{}^{} \frac{e_1^2 v_1}{2r_1} \left(\frac{1}{D_0} - \frac{1}{D}\right)$, i.e. $\Delta \bar{F}^\circ$ should vary linearly with 1/D. This has been found to be the case for lithium, sodium and potassium chloride in water and aqueous methyl alcohol solutions up to about 60 mols % alcohol;* and the same relation holds for lithium chloride in ethyl alcohol solutions.† Hydrochloric acid shows a considerable deviation when the proportion of alcohol is large, which is probably due to the ion H_3O^+ being replaced by $C_2H_5OH_2^+$ in such solutions.‡

Ionic Entropies. A valuable summary of data on ionic entropies in solution by Latimer, Hicks and Schutz (J. Chem. Phys., 2, 82, 1934) has appeared too late to be included in the text of this Chapter.

^{*} Åkerlöf, J. Amer. Chem. Soc., 52, 2353, 1930.

[†] Butler and Thomson, Proc. Roy. Soc., A, 141, 86, 1933.

[‡] Butler and Robertson, Proc. Roy. Soc., A, 125, 694, 1929.

CHAPTER IX

POTENTIAL DIFFERENCES BETWEEN PHASES CONTAINING ELECTROLYTES

Equilibrium of Ions in Different Phases. It has been shown that when two phases are in equilibrium at the same temperature and pressure, it is necessary that the partial free energy of every component which can be transferred from one phase to the other shall be the same in each phase. In deducing this relation it was assumed that no work is done against electrical forces in the transfer of small quantities of the components from one phase to the other, i.e. that the small quantities of the components which are transferred are electrically neutral. This condition is sufficient to determine the equilibrium even in systems containing electrolytes, for the ions are not independently variable components of a solution, since we cannot in practice transfer a quantity of a single ion without at the same time transferring an equivalent quantity of an oppositely charged ion. Every possible variation of the state of a salt solution can therefore be expressed by taking as the components equivalent quantities of positively and negatively charged ions suitably chosen, i.e. in terms of suitable salts.

In order to find the potential difference between two phases it is necessary, however, to consider minute trans-

fers of ions from one to the other. Let \bar{F}' , \bar{F}'' be the partial molar free energies of an ion S_a in two phases which are in equilibrium with each other, and V', V'' the electrical potentials of the two phases. If the valency of the ion is z (positive for positive ions, negative for negative ions) the electrical charge carried by a gram molecule of ions is $z\mathbf{F}$. Suppose that a small quantity dn_a mols of S_a is transferred from phase I to phase II. The change in the free energy of the system is

$$-F_a{}'dn_a+F_a{}''dn_a$$
.

The electrical work expended in transferring a charge $z_a \mathbf{F} dn_a$ from a region where the electrical potential is V' to a region where the potential is V'' is $(V'' - V')z_a \mathbf{F} dn_a$. The total work expended in the transfer is thus

$$\bar{F}_{a}{}^{\prime\prime}\,dn_{a} - \bar{F}_{a}{}^{\prime}\,dn_{a} + (V^{\prime\prime} - V^{\prime})z_{a}\mathbf{F}\,dn_{a},$$

and for equilibrium, since dn_a may be either positive or negative, this must be zero. The condition of equilibrium of the given ion in the two phases is therefore

$$\bar{F}_{a}^{\ \prime\prime} + z_{a} \mathbf{F} V^{\prime\prime} = \bar{F}_{a}^{\ \prime} + z_{a} \mathbf{F} V^{\prime}. \quad \dots (216)$$

The condition for the equilibrium of ions in a system of phases is therefore that the quantity $(\bar{F}+z\mathbf{F}V)$ for each ion must be constant throughout the system.* This quantity has thus the same properties for ions as the partial free energy has for neutral components. It has been called the "electrochemical potential" by Guggenheim.†

It can easily be shown that this condition does not conflict with the condition of equilibrium for a neutral

^{*} Butler, Proc. Roy. Soc., A, 112, 129, 1926.

[†] J. Physical Chem., 33, 842, 1929; 34, 1540, 1930; also Brönsted, Z. physikal. Chem., 143, 301, 1929.

or

salt between the two phases. Consider, for example, the distribution of sodium chloride between two liquid phases (e.g. solutions of water and ether).

Applying (216) to the equilibrium of sodium ions (z=1)

and of chloride ions (z=1), we have

$$ar{F}^{\prime\prime}{}_{\mathrm{Na^{+}}} - ar{F}^{\prime}{}_{\mathrm{Na^{+}}} = \mathbf{F}(V^{\prime} - V^{\prime\prime}), \\ ar{F}^{\prime\prime}{}_{\mathrm{Cl^{-}}} - ar{F}^{\prime}{}_{\mathrm{Cl^{-}}} = -\mathbf{F}(V^{\prime} - V^{\prime\prime}).$$

Summing, it is obvious that

$$egin{align} &ar{F}^{\prime\prime}{}_{\mathrm{Na^+}} + ar{F}^{\prime\prime}{}_{\mathrm{Cl^-}} = ar{F}^{\prime}{}_{\mathrm{Na^+}} + ar{F}^{\prime}{}_{\mathrm{Cl^-}}, \ &ar{F}^{\prime\prime}{}_{\mathrm{NaCl}} = ar{F}^{\prime}{}_{\mathrm{NaCl}}, \ \end{aligned}$$

i.e. the partial free energy of the neutral component NaCl is the same in the two phases.

The potential difference between two phases is given by

$$(V'' - V')z_a \mathbf{F} = -(\bar{F}_a'' - \bar{F}_a'). \dots (217)$$

If the absolute potential difference between two phases could be determined it would be possible to determine the difference between the partial free energies of the ions in the two phases. But there is at present no method of determining single potential differences with certainty, and it is therefore impossible to evaluate the differences of the partial free energies of individual ions in different phases. Although at present no practical use can be made of relations like (216), it is sometimes convenient and illuminating to formulate the equilibrium of systems containing electrolytes in this way.

Potential Differences in the Galvanic Cell. It is instructive to consider the equilibrium which occurs in the galvanic cell from this point of view. The electromotive force of a reversible cell can be calculated from the free energy change of the chemical reaction. The potential

difference at each phase boundary is also similarly related to the free energy change of the process occurring there. The electromotive force of the cell is the sum of the various phase boundary potentials and in the same way the free energy change of the cell reaction may be regarded as the sum of the free energy changes of the processes which occur at the various boundaries.

We will consider the cell

in which the reaction is $Zn + Cu^{++} = Cu + Zn^{++}$, neglecting entirely the non-essential liquid boundary between the two solutions. It is necessary to regard metal ions and electrons as independent components of the metal and to assign to them partial free energies, which have the same meaning as in any other phase. Let $\bar{F}_{Cu^{++}}^{(Cu)}$ and $\bar{F}_{\epsilon}^{(Cu)}$ be the partial free energies of copper ions and electrons in metallic copper and $\bar{F}_{Zn^{++}}^{(Zn)}$ and $\bar{F}_{\epsilon}^{(Zn)}$ the partial free energies of zinc ions and electrons in metallic zinc. Since zinc and copper are formed out of zinc and copper ions and electrons by the following stoichiometrical equations:

$$Zn = Zn^{++} + 2\epsilon,$$

 $Cu = Cu^{++} + 2\epsilon,$

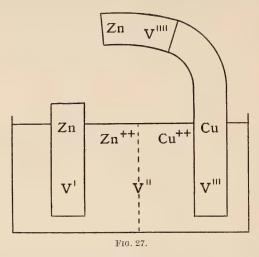
the following relations hold between the free energies of the metals and the partial free energies of the components

$$F_{\rm Zn} = \bar{F}_{\rm Zn^{++}}^{\rm (Zn)} + 2\bar{F}_{\epsilon}^{\rm (Zn)}$$

$$F_{\rm Cu} = \bar{F}_{\rm Cu^{++}}^{\rm (Cu)} + 2\bar{F}_{\epsilon}^{\rm (Cu)}$$
(218)

 $ar{F}_{\text{Cu}^{++}}^{(\text{S})}$, $ar{F}_{\text{Zn}^{-+}}^{(\text{S})}$ are the partial free energies of zinc and copper ions in the solution.

The following are the conditions of equilibrium at the various boundaries (Fig. 27).



Equilibrium of zinc ions between metal and solution:

(1)
$$2\mathbf{F}(V'-V'') = \overline{F}_{Zn^{++}}^{(S)} - \overline{F}_{Zn^{++}}^{(Zn)}$$
.

Equilibrium of copper ions between metal and solution:

(2)
$$2\mathbf{F}(V'' - V''') = \bar{F}_{Cn^{++}}^{(Cu)} - \bar{F}_{Cn^{++}}^{(S)}$$

Equilibrium of electrons between the two metals:

(3)
$$-\mathbf{F}(V^{\prime\prime\prime\prime}-V^{\prime\prime\prime}) = \overline{F}_{\epsilon}^{(\mathrm{Cu})} - \overline{F}_{\epsilon}^{(\mathrm{Zn})}.$$

Summing $(1) + (2) + 2 \times (3)$, we thus have

$$\begin{split} 2\mathbf{F}(V'-V'''') = & \, \overline{F}_{Zn^{++}}^{(\mathrm{S})} - (\overline{F}_{Zn^{++}}^{(\mathrm{Zn})} + 2\overline{F}_{\epsilon}^{(\mathrm{Zn})}) \\ & - \overline{F}_{\mathrm{Cu}^{++}}^{(\mathrm{S})} + (\overline{F}_{\mathrm{Cu}^{++}}^{(\mathrm{Cu})} + 2\overline{F}_{\epsilon}^{(\mathrm{Cu})}), \end{split}$$

or by (218),

$$2\mathbf{F}(V'-V'''')\quad F_{\mathrm{Cu}}-\bar{F}_{\mathrm{Zn}^{++}}^{\mathrm{S}}-F_{\mathrm{Zn}}-\bar{F}_{\mathrm{Cu}^{++}}^{\mathrm{S}}.$$

 $V^{\prime\prime\prime\prime} - V^{\prime} = E$ is equal to the electromotive force of the cell, and the quantity on the right is the free energy change in the cell reaction, so that we have

$$2\mathbf{F}E = -\Delta F$$

which is the usual thermodynamic relation for the complete cell.

Donnan's Membrane Equilibrium. When two solutions are separated by a membrane the equilibrium is determined by the condition that the partial free energy of every neutral component which can freely pass through the membrane must be the same on both sides. When one of the solutions contains an ion which is unable to pass the membrane, this condition, together with the condition that both solutions must remain electrically neutral, gives rise to an unequal distribution of diffusible salts on the two sides.*

We will consider the case in which aqueous solutions of (a) sodium chloride, (b) the sodium salt NaR are separated by a membrane which is permeable to sodium and chloride ions and water and impermeable to the ion R. This state of affairs occurs with parchment paper membranes when R is the anion of a heavy acid dyestuff, such as congo red, benzopurpurin. Suppose that the concentrations in the two solutions are initially

* Donnan, Z. Electrochem., 17, 572, 1911; experimental investigations by Donnan and Harris, J. Chem. Soc., 99, 1559, 1911; Donnan and Allmand, ibid., 105, 1941, 1914; Donnan and Garner, ibid., 115, 1313, 1919; Donnan and Green, Proc. Roy. Soc., A, 90, 450, 1914.

The final state of equilibrium is determined by the following considerations:

(1) The two solutions must remain electrically neutral, i.e. equal quantities of sodium and chloride ions must diffuse from one solution to the other. If we suppose that the volumes of the two solutions are equal, and that the concentrations of sodium and chloride ions on the right are reduced by diffusion to $c_1 - x$, the concentrations of sodium and chloride ions on the left will be $c_2 + x$, x. The equilibrium state may therefore be represented by

(2) For equilibrium, the partial free energy of sodium chloride must be the same in the two solutions, *i.e.*

$$\alpha_{\text{Na}+}'$$
, $\alpha_{\text{Cl}-}' = \alpha_{\text{Na}+}''$, $\alpha_{\text{Cl}-}''$,(219)

where a_{Na^+}' , a_{Na^+}'' , are the activities of sodium ion in the two solutions, etc.

In the ideal case when the activities of the ions may be supposed to be the same as their concentrations, we have

$$(c_2+x)x=(c_1-x)^2,$$
 or
$$x=\frac{{c_1}^2}{c_2+2c_1}.$$
 The ratio
$$\frac{x}{c_1}=\frac{c_1}{c_2+2c_1}$$

gives the proportion of the amount of sodium chloride originally present which has diffused through the membrane. Table XXXI gives some values of this quantity.

Initial Conc. of NaR (c_2) .	Initial Cone. of NaCl (c_1) .	$\begin{array}{c} \text{Initial} \\ \text{Ratio} \\ c_2/c_1. \end{array}$	Percentage of NaCl diffused, $x/c_1 \times 100$.	Ratio of Cl ⁻ in two solutions, x/c_1-x .
0.01	1	0.01	49.7	1.01
0.1	1	0.1	47.0	1.1
1	1 .	1	33	2
1	0.1	10	8.3	11
1	0.01	100	1	. 99

TABLE XXXI.

It can be seen that the proportion of NaCl which diffuses decreases as the proportion c_2/c_1 increases, and when this ratio is large the distribution is very unequal.

- (3) It is necessary for equilibrium that the free energy of water on the two sides of the membrane shall be equal. Since in the equilibrium state the total salt concentrations are unequal, this can only be secured by a difference of hydrostatic pressure. This difference of hydrostatic pressure is obviously equal to the difference of the osmotic pressure of the two solutions.
- (4) For the equilibrium of the ions Na⁺ and Cl⁻ it is necessary by (217), that

$$egin{aligned} ar{F}_{\mathrm{Na}^{+}}^{\prime} - ar{F}_{\mathrm{Na}^{+}}^{\prime\prime} &= &\mathbf{F}(V^{\prime\prime} - V^{\prime}), \ ar{F}_{\mathrm{Cl}^{-}}^{\prime} - ar{F}_{\mathrm{Cl}^{-}}^{\prime\prime} &= &-&\mathbf{F}(V^{\prime\prime} - V^{\prime}). \end{aligned}$$

and

There is thus a potential difference across the membrane which is given by

 $V'' - V' = \frac{RT}{F} \log \frac{\alpha_{\text{Na}^+}'}{\alpha_{\text{Na}^+}''} = \frac{RT}{F} \log \frac{\alpha_{\text{Cl}^-}''}{\alpha_{\text{Cl}^-}'}. \dots (220)$

This potential difference is equal and opposite to the difference between the potential differences of two electrodes, reversible with respect to the sodium or chloride ion, placed in the two solutions.*

* A comprehensive discussion of the thermodynamics of membrane equilibria is given by Donnan and Guggenheim, Z. phys. Chem., 162, 346, 1932.

CHAPTER X

THE THERMODYNAMICS OF SURFACES

Surface Tension and Surface Energy. We have hitherto regarded the energy or free energy of a system as the sum of the energies or free energies of its homogeneous parts, neglecting any additional energy which might be associated with the surfaces of contact between the phases. It is known that energy is associated with such surfaces, because work has to be expended to increase the surface area.

We will consider a system of two phases, separated by a boundary of area s. Let \bar{F}_1 be the partial free energy of any component, which is the same in the two phases, and n_1 the total amount present in the system. If there were no surfaces of contact the total free energy would be $F = \Sigma \bar{F}_1 n_1$, where the summation is extended over all the components. If the additional free energy associated with unit area of the surface of contact is ρ , the total free energy of the system is

$$F* = \sum \bar{F}_1 n_1 + \rho s.$$
(221)

 $\rho = \partial F * / \partial s$ is thus equal to the work which must be performed in creating unit area of new surface under reversible conditions.

Since the free energy of a system always tends to reach the smallest possible value, a mobile surface will tend to assume the minimum area which is consistent with the conditions, if ρ is positive. ρ therefore manifests itself as a contractile force, which is called the surface tension, and is usually measured in dynes per cm.² For thermodynamical purposes, however, ρ must be regarded as the surface free energy, the corresponding value of which is in ergs per cm.²

We will suppose that both phases have the same temperature T and pressure p. It will be shown below that the latter can only be the case when the radius of curvature of the surfaces is comparatively large, *i.e.* we assume that the surfaces are approximately plane. Then we may write

$$F = E - TS + pv,$$
 $F * = E * - TS * + pv *;$

where E*, S* and v* are the energy, entropy and volume of the actual system, and E, S and v the values of these when the surface area between the phases is very small. Introducing these values into (221), we have

$$F * - F + \rho s,$$
 or $E * - E = T(S * - S) - p(v * - v) + \rho s,$ or $E^s = TS^s - pv^s + \rho s.$ (222)

Here $E^s = E^* - E$ is the increase in the energy of the system consequent on the formation of the area s of surface, and S^s , v^s are similarly the corresponding increases of the entropy and volume of the system. TS^s is the heat absorbed in the reversible formation of the surface s and is the latent heat of formation of this surface. E^s , S^s and v^s may be called the surface energy, entropy and volume.

0

and

Now S^s , v^s and s in (222) are all capacity factors and T, p and ρ are intensity factors. By Euler's theorem (p. 62) it follows that the *complete* differential of E^s is

$$dE^s = TdS^s - p dv^s + \rho ds,$$

and also that the sum of the products of the capacity factors by the differentials of the intensity factors is zero, *i.e.*

$$S^{s} dT - v^{s} dp + s d\rho = 0,$$

and therefore

$$\left(\frac{d\rho}{dT}\right)_p = -\frac{S^s}{s} \dots (223)$$

and

$$\left(\frac{d\rho}{dp}\right)_T = \frac{v^s}{s},$$
(224)

i.e. the rate of change of the surface tension with the temperature is equal to minus the surface entropy of unit surface, and its rate of change with the pressure is equal to the change in volume in the formation of unit surface.

Introducing this value of S^s into (222), we have

$$\frac{E^s + pv^s}{s} = \rho - T(d\rho/dT)_p. \qquad (225)$$

The quantity $\rho - T(d\rho/dT)$ is usually regarded as the total surface energy, although strictly it is the "surface heat content." By (224), $pv^s/s = p(d\rho/dp)_T$, but little is known of the change of surface tension with pressure. Probably pv^s is comparatively small at low pressures. Values of the surface free energy, and the total surface energy $\rho - T(d\rho/dT)_p$ for the liquid-vapour interface of some liquids are given in Table XXXII. Since the surface tension decreases roughly linearly with the temperature, the total surface energy $\rho - T(d\rho/dT)_p$ remains

approximately constant over a considerable range of temperature. This is illustrated by the data for benzene in Table XXXIII.

TABLE XXXII.

Surface Tension and Total Surface Energy of Some Liquids at 0° C.

		ρ.	$-T\Big(\frac{d\rho}{dT}\Big)_p.$	$ ho - T {d \rho \choose d T}.$
Water	_	75.87	42.25	118-1
Methyl alcohol -	-	23.5	19.4	42.9
Ethyl alcohol -	-	23.99	22.39	46.4
n-Propyl alcohol	-	25.32	22.01	47.3
Hexane	-	21.31	28.15	49.5
Chloroform -	_	28.77	30.94	59.7
Carbon tetrachlorie	de -	29.35	32.84	$62 \cdot 2$

TABLE XXXIII.

TOTAL SURFACE ENERGY OF BENZENE.

ρ.	d ho/dT.	ho - d ho/dT.
20.28	-0.111	59.5
16.85	-0.1155	61.1
13.45	-0.111	59.4
9.15	-0.104	56.1
3.41	-0.087	48.1
	20·28 16·85 13·45 9·15	$\begin{array}{c ccccc} 20 \cdot 28 & & -0 \cdot 111 \\ 16 \cdot 85 & & -0 \cdot 1155 \\ 13 \cdot 45 & & -0 \cdot 111 \\ 9 \cdot 15 & & -0 \cdot 104 \end{array}$

*Equilibrium at Curved Surfaces. The equilibrium of systems containing interfaces is most conveniently investigated by means of Gibbs's second criterion of equilibrium, viz.,

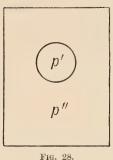
$$(\delta E)_s \ge 0$$
;

i.e. the system is in equilibrium when none of the possible changes it may undergo at constant entropy can decrease its energy. The condition of constant entropy is satisfied

if we ensure that no heat may leave or enter the system under investigation.

When the contribution of the interface to the energy of the system is neglected we have found the conditions of equilibrium between any two phases are:

- (1) the temperature and pressure must be the same;
- (2) the partial free energy of every neutral component must be the same in both phases. The surface energy



can quite properly be neglected when the homogeneous phases are large compared with their surfaces, but when the phases are very small it is no longer possible to neglect this factor, since a small transfer of material from a small body may appreciably change its surface area.

We will consider a small sphere of a liquid in contact with its vapour (Fig. 28). Let the free energy of the liquid, including the

interfacial free energy, be F'. Then $F' = \bar{F}' n_1' + \rho s$ or $E' = TS' - p'v' + \overline{F}'n_1' + \rho s$, where E', S', v' are the corresponding energy, entropy and volume. Similarly if E'', S'', v'' are the energy, entropy and volume of the vapour we have

$$E'' = TS'' - p''v'' + \bar{F}_1''n_1''.$$

The variations of E' and E'' are thus expressed by

$$dE' = T dS' - p'dv' + \bar{F}_1'dn_1' + \rho ds,$$

 $dE'' = T dS'' - p''dv'' + F''dn_1''.$

The condition of equilibrium is that $(dE' + dE'') \ge 0$ for all possible variations in which the total entropy remains constant, i.e. dS' + dS'' = 0. We will also suppose that the total volume is constant, i.e. dv' + dv'' = 0. Then, since it is also necessary that $dn_1' + dn_1'' = 0$,

$$dE' + dE'' = -(p' - p'')dv' + (\bar{F}' - \bar{F}'')dn_1' + \rho ds \ge 0.$$

The conditions of equilibrium are thus

or

$$\bar{F}_{1}{}' = \bar{F}_{1}{}'', *$$

and since we cannot increase the volume of the sphere without changing its area, and dv' may be either positive or negative:

$$-\left(p'-p''\right)\,dv'+\rho\,ds=0,$$

$$p'-p''=\rho\,\frac{ds}{dv'}.$$

If the radius of the sphere is r, $v' = \frac{4\pi}{3}r^3$ and $s = 4\pi r^2$, and it can easily be shown that ds/dv' = 2/r. The pressure difference inside and outside the sphere is thus

$$p' - p'' = 2\rho/r, \dots (226)$$

the pressure being always greatest inside the concave surface.

This increase of pressure causes an increase of the partial free energy of the liquid, which can be calculated by (142), i.e. $d\bar{F}' = \bar{v}_1'dp'$, where \bar{v}_1' is the partial molar volume in the liquid. Neglecting the change of p'', we have $dp' = d(2\rho/r)$, and integrating on the assumption that ρ is constant, we find that

$$(\bar{F}_{1}')_{r} = (\bar{F}_{1}')_{\infty} + 2\bar{v}_{1}\rho/r,$$

where $(\bar{F}_1)_r$ and $(\bar{F}_1)_{\infty}$ are the partial free energies of the liquid in a droplet of radius r and at a plane surface,

^{*} dn_1 ' may be positive or negative without affecting the other variables, i.e we may pack a few more molecules into the sphere, keeping its volume constant, or take them away.

since the partial free energy in the vapour remains equal to that in the liquid, the vapour pressure of the liquid must increase as r diminishes. Since

$$(\overline{F}_1)_r - (\overline{F}_1)_{\infty} = RT \log[(p_1{}^r/p_1{}^{\infty}),$$

the magnitude of this effect is given by

$$RT \log (p_1^r/p_1^{\infty}) = \frac{2\bar{v}_1 \rho}{r}, \dots (227)$$

where p_1^r and p_1^{∞} are the vapour pressures in a droplet of radius r and at a plane surface.* For water at room temperature ($\rho = \text{ca. } 70 \text{ dynes/cm.}$), the pressure in a droplet of radius 10⁻⁵ cm. is about 14 atmospheres, and its vapour pressure is thereby increased about one per cent.† At concave surfaces a similar decrease of the vapour pressure is predicted. A similar relation in which the ratio of the solubilities takes the place of the ratio of the vapour pressures can be obtained for the effect of particle size on the solubility of solids and liquids. This has been employed to measure ρ at solidliquid interfaces.‡ Values between 10 and 3000 ergs per cm. have been obtained for comparatively insoluble salts, but their validity is uncertain because ρ , which has been assumed constant, may vary with the particle size, and the radius of curvature of solid particles may vary from point to point.

Equation (226) can also be used to find the capillary rise in narrow tubes. When the radius of the tube is

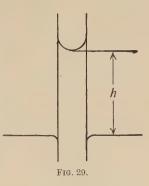
^{*} This equation was first obtained by Lord Kelvin (W. Thomson), *Phil*, *Mag.*, **42**, 448, 1881.

[†] Shereshevski, J. Amer. Chem. Soc., 50, 2966, 2980, 1928, found a somewhat greater change than is predicted by this equation.

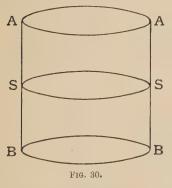
[‡] W. Ostwald, Z. physik. Chem., **34**, 495, 1900; Dundon, J. Amer. Chem. Soc., **45**, 2479, 2658, 1923.

sufficiently small the meniscus is practically a hemisphere. The pressure difference on the two sides of the surface is

balanced by the hydrostatic pressure of the column of liquid (Fig. 29), which is approximately given by (h+r/3)dg, where h is the height of the column from the plane surface outside the tube to the lowest point of the meniscus, r/3 is a correction for average height above the lowest point of the meniscus, and the difference between the density of the



liquid inside the tube and the gas outside, and g the force of gravity. Introducing this value into (226), we have



$$(h+r/3)gd = 2\rho/r.$$

When r is large the surface ceases to be hemispherical, and this equation needs considerable correction.*

Gibbs's Absorption Equation. Let SS (Fig. 30) be part of the interface between two phases. The two surfaces AA, BB are now drawn within the

homogeneous phases on each side of the interface at a sufficient distance so that they contain between them the

* Cf. Sugden, J. Chem. Soc., 1921, p. 1483; Rayleigh, Proc Roy. Soc., A, 92, 184, 191. whole of the parts which are influenced by the vicinity of the interface. A surface AB - AB is also drawn perpendicular to the interface, enclosing part of it. The closed surface so formed contains part of the interface, together with portions of the homogeneous phases. suppose that the volume within this closed surface is constant. It can easily be shown that the conditions necessary for equilibrium in this system are: (1) the temperature must be constant throughout, (2) the partial free energy of each component is the same in the two homogeneous phases and in the region between AA and BB. This can be proved by the method previously used, and holds true provided there is no condition limiting the transfer of small quantities of any component in or out of either part of the system. Thus if the region between AA and BB contains n_1 mols of S_1 , n_2 mols of S_2 , etc., we suppose that dn_1 , dn_2 , etc., can separately be made either positive or negative. The case does not differ then in any essential respect from the equilibrium of three separate phases in contact—every component must have the same partial free energy in each phase.

The total free energy of the volume enclosed between AA and BB is therefore

$$F = \overline{F}_1 n_1 + \overline{F}_2 n_2 + \overline{F}_3 n_3 \dots + \rho s, \dots (228)$$

where \overline{F}_1 is the partial free energy of S_1 throughout the system, etc., ρ the additional free energy of unit area of the interface and s its area. Writing F = E - TS + pv, and remembering that v is constant, the variation of the energy is given by

$$dE = T dS + \overline{F}_1 dn_1 + \overline{F}_2 dn_2 + \dots + \rho ds.$$

All the differentials in this equation are capacity factors, and as before it follows from Euler's theorem that

$$S dT + n_1 d\bar{F}_1 + n_2 d\bar{F}_2 \dots + s d\rho = 0. \dots (229)$$

Now, in this equation n_1 , n_2 , etc., are quite indefinite quantities, for they depend on the amounts of the homogeneous phases which have been included in the volume between the surfaces AA, BB. In order to obtain an equation which contains quantities which are characteristic of the interface we proceed as follows. Another surface is drawn near the actual interface, the exact position of which is as yet undetermined. Let it be supposed that the homogeneous phases continue without any change of composition or of properties on either side up to this dividing surface. Let the quantities of the components in the volume between AA and BB in this hypothetical case be n_1' , n_2' , n_3' , etc., on one side of the dividing surface and $n_1^{\prime\prime}$, $n_2^{\prime\prime}$, $n_3^{\prime\prime}$, etc., on the other, and the corresponding quantities of entropy S', S''. Then since these hypothetical masses have the properties of the two homogeneous phases it follows that

$$S' dT + n_1' d\bar{F}_1 + n_2' d\bar{F}_2 \dots = 0,$$

 $S'' dT + n_1'' d\bar{F}_1 + n_2'' d\bar{F}_2 \dots = 0.*$

Subtracting these equations from (229), we obtain

$$(S - S' - S'') dT + (n_1 - n_1' - n_1'') d\overline{F}_1 + (n_2 - n_2'' - n_2'') d\overline{F}_2 \dots + s d\rho = 0,$$

$$S^s dT + n_1^s d\overline{F}_1 + n_2^s d\overline{F}_2 \dots + s d\rho = 0, \dots \dots (230)$$

* For a homogeneous phase,

or

$$E = TS + \overline{F}_1 n_1 + \overline{F}_2 n_2 \dots - pv,$$
 and, therefore,
$$dE = TdS + \overline{F}_1 dn_1 + \overline{F}_2 dn_2 \dots - pdv,$$
 and
$$SdT + n_1 d\overline{F}_1 + n_2 d\overline{F}_2 \dots - vdp = 0.$$

where $S^s = S - S' - S''$ is the difference between the actual entropy of the given volume and that which would be present on the assumption that the homogeneous phases continue without change up to the dividing surface; $n_1^s = n_1 - n_1' - n_1''$ is the corresponding difference in the amounts of the component S_1 , etc.

Dividing through by s, we have then for unit area of interface

$$\begin{array}{ll} \mathbf{s}^s\,d\,T + \Gamma_1\,d\,\bar{F}_1 + \Gamma_2\,d\,\bar{F}_2 + \Gamma_3\,d\,\bar{F}_3\,\dots + d\rho = 0,\,\,\dots (231)\\ \text{where} & \mathbf{s}^s = S^s/s,\,\,\Gamma_1 = n_1{}^s/s,\,\,\Gamma_2 = n_2{}^s/s,\,\,\text{etc.} \end{array}$$

The values of Γ_1 , Γ_2 , etc., which are called the *surface* excesses of S_1 , S_2 , etc., still depend on the position of the dividing surface. The latter can therefore be placed in such a position as to make any one of these quantities zero. If the dividing surface is so placed that $\Gamma_1 = 0$, we then have

$$\mathbf{s}^{s} dT + \Gamma_{2} d\bar{F}_{2} + \Gamma_{3} d\bar{F}_{3} \dots + d\rho = 0. \dots (232)$$

This is Gibbs's absorption equation. In succeeding sections we shall give illustrations of its application in particular cases.

Absorption from Binary Solutions. Applied to the liquid-vapour surface of a binary solution, when the dividing surface is placed so that $\Gamma_1=0$, (232) becomes at constant temperature

$$\Gamma_2 = -\left(d\rho/d\bar{F}_2\right)_T.$$

Writing $\vec{F}_2 = \vec{F}^{\circ}_2 + RT \log a_2$, where a_2 is the activity of S_2 , we have then

$$\Gamma_2 = -\frac{1}{RT} \left(\frac{d\rho}{d\log a_2} \right)_T.$$
(233)

 Γ_2 is the surface excess of S_2 , *i.e.* the difference between the actual amount of S_2 present in a given volume

including the interface and that which would be present if the phases were perfectly homogeneous up to a dividing surface placed so that $\Gamma_1 = 0$. According to (233), when $d\rho/d\log a_2$ is negative, i.e. when the surface tension decreases with increasing activity of S_2 , Γ_2 is positive; and when $d\rho/d \log a_2$ is positive, Γ_2 is negative. A substance which lowers the surface energy is thus present in excess at or near the surface, but there is a deficit of a substance which increases the surface energy. This is in accordance with the general thermodynamical principle that the free energy of a system tends to reach a minimum value.

 ρ is usually measured as a surface tension in dynes per cm. The corresponding surface energy is in ergs/cm. In calculating Γ_2 it is necessary to use the value of R in ergs (viz. $1.988 \times 4.182 \times 10^7$ ergs). We thus have

$$\Gamma_2 = -\frac{1}{2\cdot 303\times 1\cdot 988\times 4\cdot 182\times 10^7 T} \Big(\frac{d\rho}{d\log_{10}\alpha_2}\Big),$$

which gives I', in gm. molecules per cm.2 In order to obtain the number of molecules per cm. it is necessary to multiply this by the Avogadro number $N_0 = 6.062 \times 10^{23}$. At 25° we thus obtain

$$\Gamma_{\rm 2} = -1.062 \times 10^{13} (d\rho/d\log_{10}\alpha_{\rm 2})~{\rm molecules/cm.^2}$$

 $d\rho/d\log_{10}\alpha_2$ can be obtained by plotting ρ against $\log_{10}\alpha_2$ and finding the slope of the curve. Fig. 31 shows this plot for n-butyl alcohol solutions. When a considerable number of points are available $d\rho/d\log\alpha_2$ may be evaluated as

$$\Delta \rho / \Delta \log \alpha_2$$

for the intervals between successive points. This gives the average value of Γ_2 for the interval. Table XXXIV shows the calculation of Γ_2 for n-butyl alcohol in aqueous solution at 25°.* The activities of butyl alcohol at 25° were taken

^{*} Harkins and Wampler, J. Amer. Chem. Soc., 53, 850, 1931.

as equal to their values at the freezing point as determined by the freezing point method (see p. 99).

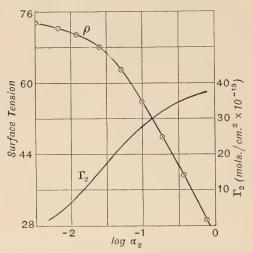


FIG. 31.—Surface tension and adsorption of butyl alcohol solutions at 25°.

TABLE XXXIV. Adsorption at Surface of Butyl Alcohol Solutions, 25° .

m_2 .	a_2 .	ρ.	Γ_2 (molecules/cm.2)
0.00329	0.00328	72.80	
0.00658	0.00654	$72 \cdot 26$	_
0.01320	0.01304	70.82	0.76×10^{14}
0.0264	0.02581	68.00	1.31
0.0536	0.05184	$63 \cdot 14$	$2 \cdot 14$
0.1050	0.09892	56.31	2.86
0.2110	0.19277	48.08	3.19
0.4330	0.37961	38.87	3.45
0.8540	0.71189	29.87	3.65

The Gibbs equation does not measure the total number of solute molecules in or near the surface, but the surface excess. In dilute solutions, however, the number of solute molecules which would be present near the surface if the phases were perfectly homogeneous up to the interface is comparatively small, and Γ_2 does not differ appreciably from the actual number of molecules in or near the interface. In the stronger solutions Γ_2 approaches the value required for a single complete layer of alcohol molecules orientated with their hydrocarbon chains vertical.*

The activities of few non-electrolytes in aqueous solution have been accurately determined. In dilute solutions an approximate measure of Γ_2 , which will probably not be considerably out, may be obtained by replacing a_2 by m_2 in (233). In concentrated solutions, however, a large error may occur unless the actual activity is used. Fig. 32 shows the values of ρ plotted against $\log m_2$ for solutions of homologous normal fatty acids. Taking Γ_2 as the slope $-d\rho/RT d \log m_2$, it can be seen that approximately the same value is reached in every case, but as we go up the series of acids this value is reached at a progressively lower concentration. The final value of Γ_2 corresponds approximately with a nearly completed surface layer of molecules orientated with their hydrocarbon chains vertical.

Tests of Gibbs's Equation. It is unnecessary to describe here the earlier attempts to confirm Gibbs's equation by the direct determination of the surface excess of a solute at an interface.

^{*} According to N. K. Adam's measurements of the areas of molecules in insoluble surface films the area of molecules of long chain aliphatic alcohols when tightly packed is 21.7×10^{-16} cm.², corresponding to about 46×10^{18} molecules per cm.²

[†] e.g. Donnan and Barker, Proc. Roy. Soc., A, 85, 57, 1911.

McBain with Davies * and Du Bois † passed bubbles of nitrogen through solutions of surface active substances in an inclined tube. These carried thin films of the solution up the outlet tube, which after being allowed to drain of their excess liquid were collected. The excess

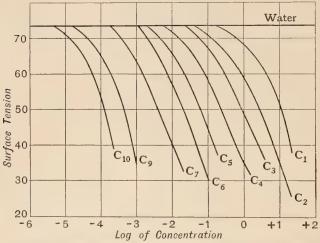


Fig. 32.—Surface tensions of solutions of normal aliphatic acids plotted against logarithm of concentration, (Harkins.)

of solute in unit area of surface could be calculated from a determination of the concentration of the solute in the condensed films and of their area. The values of the surface excess so obtained were always considerably greater than those calculated for the same solutions by Gibbs's equation. More recently McBain and Humphreys; have invented a "microtome" method in which

^{*} J. Amer. Chem. Soc., 49, 2230, 1927.

[†] *ibid.*, **51**, 3534, 1929.

[‡] Colloid Symposium Monograph, ix. 300, 1931.

a thin film at the surface of a solution is skimmed off the surface of a solution by a rapidly moving blade, and the difference between its concentration and that of the bulk of the solution is determined. The surface excesses measured by this method, which are given in Table XXXV, are in reasonable agreement with those calculated by Gibbs's equation, considering the difficult nature of the experiments.

TABLE XXXV. OBSERVED AND CALCULATED SURFACE EXCESSES OF AQUEOUS SOLUTIONS.

Substance.	Conc. of solute $g/1000g.H_2O.$	$\begin{array}{c c} Surface\ excess\\ \Gamma_2\ obs.\\ g/cm.^2\times 10^8. \end{array}$	r. calc. by Gibbs's equation.	T obs. by Bain and Du Bois.
p-Toluidine	2·00 1·76	6·1 4·6	5·2 4·9	11.8
Phenol	20.5	4.1	4.8	14.8
Caproic acid	$2.59 \\ 3.00 \\ 5.25$	$6.8 \\ 5.1 \\ 6.2$	$6.3 \\ 6.5 \\ 6.3$	$16.2 \\ 16.9 \\ 20.5$
Hydrocin- namic acid	1.5 4.5	5·6 5·4	5·1 7·9	_

It is possible that high values are obtained in the bubbling experiments, because water molecules can drain out of the films more easily than the larger solute molecules. Accordingly, when the films are allowed to drain before collection, the liquid between the surface layers of the film becomes more concentrated than the bulk of the solution and therefore too large a value of the surface excess is obtained.

Surface of Aqueous Solutions of Salts. Since inorganic salts increase the surface tension of water they are negatively absorbed. It is more convenient in such a case to place the dividing surface so that the surface excess of the salt (Γ_2) is zero.

The surface excess of water (Γ_1) is then given by

$$\Gamma_1 = -d\rho/d\bar{F}_1.$$

The variations of the partial free energies of water and the salt are related by $n_1 d\bar{F}_1 + n_2 d\bar{F}_2 = 0$; and the variation of the partial free energy of the salt is given by $d\bar{F}_2 = (\nu_1 + \nu_2)RTd\log a_\pm$, where a_\pm is its mean activity. For a binary salt we therefore have

$$\Gamma_1 = -\frac{d\rho_1}{dF_1} = +\frac{n_1}{n_2} \frac{d\rho}{2RT \log a_{\pm}}.$$
(234)

If the solution contains m_2 mols of a salt to 1000 gms. (55·55 mols) of water $n_1/n_2 = 55 \cdot 55/m_2$, and writing $d \log \alpha_{\pm} = d\alpha_{\pm}/\alpha_{\pm}$ and $\alpha_{\pm} = m_2 f_{\pm}$, we have

$$\Gamma_1 = \frac{55 \cdot 55 f_{\pm}}{2RT} \left(\frac{d\rho}{da_{\pm}} \right).$$

Table XXXVI shows the adsorption of water at the surface of sodium chloride solutions as determined by Harkins and McLaughlan.*

TABLE XXXVI.

Adsorption of Water at Surface of Sodium Chloride Solutions,

It can be seen that Γ_1 decreases as the solution becomes more concentrated, indicating that the ions approach the

* J. Amer. Chem. Soc., 47, 2083, 1925; also 48, 604, 1926. Cf. Goard, J. Chem. Soc., 2451, 1925.

surface more closely in concentrated solutions. Assuming that the density in the absorbed layer is the same as that of liquid water d=1, and that the absorbed layer and the solution meet sharply at the dividing surface, Γ_1 (expressed in gms./cm.²) is equal to the thickness of the absorbed layer. The diameter of the water molecule in ice and crystalline hydrates is 2.76×10^{-8} cm., so that it would appear that the thickness of the film in the strong solutions is of the same order as the diameter of the water molecule.

Adsorption from Ternary Solutions. In a system containing three components, at constant temperature, (231) becomes

$$\Gamma_1 d\overline{F}_1 + \Gamma_2 d\overline{F}_2 + \Gamma_3 d\overline{F}_3 + d\rho = 0,$$

where Γ_1 , Γ_2 , Γ_3 are the surface excesses of the components with respect to an arbitrarily fixed dividing surface. As before, it is possible to place this dividing surface so that one of these quantities is zero. If we make $\Gamma_3 = 0$ in this way, we then have

$$\Gamma_1 d\bar{F}_1 + \Gamma_2 d\bar{F}_2 + d\rho = 0.$$

A single equation of this kind is, however, insufficient to determine the values of Γ_1 and Γ_2 .* But it is always possible to vary the composition of a given ternary solution in two distinct ways.

* A considerable number of calculations of the adsorption in ternary solutions are to be found in the literature, which employ the simple Gibbs's equation $d\rho/d\bar{F}_2 = \Gamma_2$; e.g. Seith, Z. physikal. Chem., 117, 257, 1925; Freundlich and Schnell, ibid., 133, 151, 1928; Palitzsch, ibid., 147, 51, 1930.

Actually $d\rho/d\overline{F}_2 = \Gamma_2 + \Gamma_1 (dF_1/d\overline{F}_2)$, i.e. the equation for a binary solution, is not applicable unless either

$$\Gamma_1 = 0$$
, or $d\overline{F}_1/d\overline{F}_2 = 0$.

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Thus, (1) the quantity S_3 may be kept constant and the proportions of S_1 and S_2 varied; (2) the quantities of S_1 and S_2 may be kept constant and the amount of S_3 varied. For these variations we obtain two distinct equations, viz.,

$$\begin{split} &\Gamma_{1}d\bar{F}_{1}+\Gamma_{2}d\,\bar{F}_{2}+d\rho=0,\\ &\Gamma_{1}d\bar{F}_{1}{'}+\Gamma_{2}d\bar{F}_{2}{'}+d\rho{'}=0. \end{split}$$

Solving these equations for Γ_1 and Γ_2 , we obtain

These equations have been applied by Butler and Lees* to the surfaces of solutions of lithium chloride in water-ethyl alcohol mixtures. In this case, let S_1 be water, S_2 alcohol, and S_3 lithium chloride. $d\rho$, $d\bar{F}_1$ and $d\bar{F}_2$ refer to variations in which the quantity of lithium chloride is kept constant and the proportions of water and alcohol are varied. $d\bar{F}_1$, $d\bar{F}_2$ are given by the values of $RTd\log p_1$ and $RTd\log p_2$ corresponding to these variations. Similarly $d\rho'$, $d\bar{F}_1'$, $d\bar{F}_2'$ refer to variations in which the quantities of water and alcohol are kept constant and the amount of lithium chloride is varied, and

$$d\bar{F}_{1}{}' = RTd \log p_{1}{}', \quad d\bar{F}_{2}{}' = RT d \log p_{2}{}'.$$
* J. Chem. Soc., 2097, 1932.

Inserting these values, we have

$$\Gamma_2 = \frac{d\rho/RT \cdot d \, \log \, p_2 - d\rho'/RT \cdot d \, \log \, p_2'}{d \, \log \, p_1'/d \, \log \, p_2' - d \, \log \, p_1/d \, \log \, p_2}, \, \text{etc.} \quad (236)$$

Table XXXVII shows the average values of Γ_1 and Γ_2 in molecules per cm.2, as determined in this way for solutions containing from 0 to 0.5m lithium chloride. These figures may be taken to represent the composition of the surface film which contains no lithium chloride.

 Γ_2 in all the solutions corresponds approximately with a single layer of alcohol molecules, while Γ_1 diminishes steadily as the proportion of alcohol in the solution is increased. It is thus probable that at the surface of the fairly dilute alcoholic solutions there is a nearly complete monomolecular layer of alcohol molecules, but the ions are separated from this by a certain thickness of water, owing probably to their hydration. As the proportion of alcohol in the solution is increased the ions are solvated by water to a decreasing extent and the ions are able to approach the surface film of alcohol molecules more closely.

TABLE XXXVII.

ADSORPTION AT SURFACE OF WATER-ALCOHOL SOLUTIONS CONTAINING LITHIUM CHLORIDE (LiCl, 0 TO 0.5m).

Composition of Solvent (Mols % Alcohol).	$\mathbf{r}_{\scriptscriptstyle{1}}$.	Γ_2 .
0.0	133×10^{13}	
$egin{array}{c} 6 \cdot 4 \ 25 \end{array}$	103 53	42×10^{13} 57
50	15	40
80 100	$\frac{4 \cdot 6}{0 \cdot 0}$	$\begin{array}{c} 34 \\ 41 \end{array}$

Adsorption from Concentrated Solutions. Relation between Gibbs's Surface Excess and the Surface Composition. In a concentrated solution the surface excess of the solute, as determined by Gibbs's equation, may be considerably less than the actual amount in or near the surface, for even if the solution were perfectly homogeneous up to the boundary there would be an appreciable amount of the solute in or near the surface. This

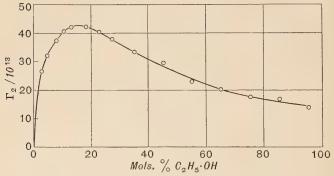


FIG. 33.—Surface excess of alcohol in water-alcohol solutions. (Butler and Wightman.)

is borne out by calculations of the surface excess in concentrated solutions. For example, the calculation of the surface excess of alcohol (Γ_2) in water-alcohol solutions is given in Table XXXVIII. The average value of Γ_2 for the interval between one solution and the next is given by $\Gamma_2 = -\Delta\rho/RT\Delta\log p_2$.*

In Fig. 33 the values of Γ_2 are plotted against the molar fraction of alcohol in the solution. They rise to a maximum in the solution containing about 15 mols %

^{*}This equation was first employed by Schofield and Rideal, *Proc. Roy. Soc.*, A, 109, 57, 1925.

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alcohol, and gradually decrease as the proportion of alcohol in the solution is further increased.

TABLE XXXVIII. CALCULATIONS OF SURFACE EXCESS OF ALCOHOL (Γ_2) IN WATER-ETHYL ALCOHOL SOLUTIONS AT 25°.

Mols % Alcohol.	ρ.	$\log_{10}p_2$.	Γ_2 .
100	21.93	1.771	
90	22.59	1.722	14.0×10^{13}
80	23.26	1.679	16.5
70	23.93	1.639	17.5
60	$24 \cdot 67$	1.600	20.4
50	25.43	1.565	23.0
40	26.43	1.529	29.5
30	27.60	1.492	33.5
25	28.49	1.467	37.8
20	29.97	1.428	40.3
15	32.20	1.372	42.3
12	34.42	1.316	$42 \cdot 2$
$\overline{10}$	36.72	1.256	40.7
6.4	42.13	1.097	37.2
4	47.86	0.908	$32 \cdot 2$
2	55.57	0.602	26.8

It might be expected that the surface excess would gradually diminish as the proportion of alcohol in the solution is increased, if the total amount of alcohol in or near the surface remained constant or increased only slowly. But it would be impossible to deduce from the values of Γ_2 the actual distribution of water and alcohol molecules near the surface if nothing were known as to how the surface excess is distributed. There is, however, a considerable amount of evidence in favour of the view that the forces which cause adsorption have a very short range and that their influence does not extend beyond the surface layer of molecules. If we make the assumption that the solution is quite homogeneous up to the

surface layer and that only in the surface layer of molecules is the proportion of alcohol different to that in the bulk of the solution, it becomes possible to determine the surface composition.*

Let v_1 , v_2 be the actual number of molecules of S_1 , S_2 in unit area of the surface layer of a binary solution. If A_1 , A_2 are the areas per molecule, we have

$$A_1v_1 + A_2v_2 = 1.$$
(237)

Now suppose that the surfaces AA, BB (Fig. 30) are brought together so that they contain between them only the surface layer of molecules which is defined by (237). On the assumption which has been made the phases outside these surfaces still remain perfectly homogeneous. Applying (229) to the matter between the surfaces, we have then, at constant temperature,

$$v_1 d\bar{F}_1 + v_2 d\bar{F}_2 + d\rho = 0.\dagger...(238)$$

Now if N_1 , N_2 are the molar fractions of S_1 , S_2 in the solution, we also have

$$N_{1}\,d\bar{F}_{1}+N_{2}\,d\bar{F}_{2}=0,$$

and substituting for $d\bar{F}_1$ in (238), we obtain

$$\left(v_2 - \frac{v_1 N_2}{N_1}\right) d\tilde{F}_2 + d\rho = 0.$$
 (239)

Since $-d\rho/d\bar{F}_2 = \Gamma_2$ is the Gibbs's surface excess, it follows that

$$\Gamma_2 = \nu_2 - \nu_1 N_2 / N_1 \dots (240)$$

* Butler and Wightman, J. Chem. Soc., 1932, p. 2089. Cf. Guggenheim and Adam (Proc. Roy. Soc., A, 139, 218, 1932).

† The unit of quantity here is the molecule, instead of the gm. molecule as previously. $\vec{F_1}$, $\vec{F_2}$ must be the partial free energy per molecule.

A physical meaning can easily be given to this equation. The surface layer contains ν_2 molecules of S_2 and ν_1 molecules of S_1 . If the proportions of S_1 and S_2 were the same in the surface layer as in the bulk of the solution, ν_1 molecules of S_1 would be accompanied by $\nu_1 N_2/N_1$ molecules of S_2 . The surface excess of S_2 is therefore $\nu_2 - \nu_1 N_2/N_1$.

Substituting $v_2 = (1 - A_1 v_1)/A_2$, we obtain

$$\Gamma_2 \!=\! \frac{1}{A_2} \!-\! \left(\! \frac{A_1}{A_2} \!+\! \frac{N_2}{N_1} \!\right) \nu_1 \!\!\!\! . \quad \dots \dots \dots (241)$$

If we know A_1 and A_2 , it is possible to find v_1 , and therefore also v_2 .

Butler and Wightman found that when A_1 and A_2 were given any reasonable values, ν_2 did not increase continuously as the proportion of alcohol in the solution increased, but went through a small maximum. Since it is very probable that as the alcohol content of the solution increases the proportion of alcohol in the surface layer will also increase, it thus appears that the fundamental assumption that only the surface layer differs from the bulk of the solution is incorrect. The difference between the observed values of the surface excess and those which would be consistent with a surface layer characterised by (257) is, however, small. The difference can be accounted for if it is supposed either that there is a small excess of alcohol molecules below the surface layer in the neighbourhood of the maximum adsorption, or by an excess of water below the surface layer in more concentrated solutions. The latter is perhaps the more probable. Schofield and Rideal have indeed suggested that the whole of the decrease in Γ_2 in strong solutions is to be accounted for in this way.* But this involves the

^{*} Phil. Mag., 13, 806, 1932.

assumption that there is no water in the surface layer itself.

This discussion will serve to illustrate the difficulties which arise when we attempt to deduce the actual distribution of molecules near the interface from the Gibbs's surface excess. The latter is a thermodynamical quantity which is exactly defined and can be accurately evaluated. If the distribution of the surface excess about the interface is known, it is possible to deduce the actual distribution of molecules. Since there is no direct way of determining this distribution, the validity of the distribution of molecules which is arrived at depends on the truth of the particular assumptions on which it is based.

Relations between Adsorption, Surface Tension and Concentration. Gibbs's equation by itself does not give any relation between the surface tension and the activity of a solute. If, however, the adsorption is known as a function of the activity of the solute, it is possible to calculate the surface tension, for since

$$\Gamma_2 = -d\rho/RT d \log a_2,$$

$$\rho = \rho_0 - RT \int_0^{a_2} \Gamma_2 \cdot d \log a_2, \dots (242)$$

where ρ_0 is the surface tension of the solvent.

Langmuir obtained by a kinetic argument a relation of this kind for the adsorption of a gas at the surface of a solid. The surface is supposed to consist of a number of spaces, each of which can accommodate a molecule of the gas. Let there be N such spaces in unit area of the surface, and at equilibrium suppose that a fraction θ of them is occupied by gas molecules. The rate of

adsorption of the gas will be proportional to its pressure and to the number of unoccupied spaces, i.e. to $N(1-\theta)p$, and the rate at which adsorbed molecules leave the surface to the number of occupied spaces, $N\theta$. For equilibrium the rates of adsorption and of desorption must be equal, so that $kN(1-\theta)p=N\theta$, or $\theta/(1-\theta)=kp$, where k is a constant which depends on the temperature.

A similar equation may be obtained for equilibrium at the surface of a solution. If the surface layer contains ν_2 solute molecules each of area A_2 , the fraction of the surface occupied by the solute is $A_2\nu_2$ and the fraction occupied by the solvent $1 - A_1\nu_1$.

If we suppose that the rate at which solute molecules enter the surface layer is proportional to the fraction of the surface unoccupied by solute molecules and to the activity of the solute, and the rate at which they leave it to the fraction occupied, we shall have for equilibrium

$$\frac{A_2^{\nu_2}}{1 - A_2^{\nu_2}} = ka_2, \quad \dots (243)$$

or
$$A_2 \nu_2 = \frac{k a_2}{1 + k a_2}$$
.(244)

In dilute solutions ν_2 may be taken as equal to Gibbs's surface excess Γ_2 . The following table shows the values of ν_2 for butyl alcohol calculated by this equation, compared with the values of Γ_2 determined by Gibbs's equation by Harkins and Wampler. The agreement is very good.*

^{*} It should be stated that the agreement is not so good in more dilute solutions. (See Butler, *Proc. Roy. Soc.*, A, 135, 348, 1932.)

TABLE XXXIX.

Adsorption from Butyl Alcohol Solutions.

$$k = 34$$
, $1/A_2 = 3.75 \times 10^{14}$.

a_2 .	ν ₂ (calc.).	Γ_2 ,
0.0989	2.89×10^{14}	2.86×10^{14}
0.1928	3.18	3.19
0.3796	3.47	3.45
0.7119	3.60	3.65
oc	3.75	

If we use for Γ_2 the value of ν_2 given by (244), we have

$$\rho = \rho_0 - \frac{RT}{A_2} \int_0^{a_2} \frac{ka_2}{1 + ka_2} \cdot d \log a_2$$

$$= \rho_0 - \frac{RT}{A_2} \log_e (1 + ka_2). \dots (245)$$

Szyszkowski found empirically that a similar equation, viz.

$$\rho = \rho_0 - a \log (1 + kc_2),$$

represented fairly closely the surface tensions of aqueous solutions of the normal fatty acids, the constant a being nearly the same for all and k increasing in an approximately constant ratio as we pass up the series.* Traube had found in the course of his extensive researches on the surface tensions of solutions that the concentrations of compounds of a homologous series, such as the normal aliphatic acids, which cause the same lowering of the surface tension of water, decrease progressively and in an approximately constant ratio as we pass up the series. Expressed in terms of Szyszkowski's equation, this implies that for compounds having the same value of a,

^{*} Z. Phys. Chem., 64, 385, 1908.

the constant k increases in a constant ratio as we pass from one member of a homologous series to the next. The average value of this ratio for the fatty acids is 3.5. Its meaning is considered in a later section.

Solutions containing two or more solutes. The same method can be applied to the simultaneous adsorption of more than one solute.* If unit area of the surface layer contains ν_2 molecules each of area A_2 of the solute S_2 , and ν_3 molecules each of area A_3 of the solute S_3 , the fraction of the surface occupied by the solvent is

$$1 - A_1 \nu_1 - A_2 \nu_2,$$

and for the kinetic equilibrium of the surface layer with the solution the following relations must be satisfied.

$$\begin{split} \frac{A_2\nu_2}{1-A_2\nu_2-A_2\nu_2} = & k_2a_2, \\ \frac{A_3\nu_3}{1-A_3\nu_2-A_3\nu_2} = & k_3a_3. \end{split}$$

Solving these equations for ν_2 , ν_3 , it is found that

$$\begin{split} \nu_2 = & \frac{1}{A_2} \left(\frac{k_2 a_2}{1 + k_2 a_2 + k_3 a_3} \right), \\ \nu_3 = & \frac{1}{A_3} \left(\frac{k_3 a_3}{1 + k_2 a_2 + k_3 a_3} \right). \quad \dots (246) \end{split}$$

Now if we take a solution of S_2 alone, which has the surface tension ρ' and add S_3 until its activity is α_3 , the surface tension of the resulting solution, assuming that the activity of S_2 is unaffected by the addition of S_3 , is

$$\rho = \rho' - RT \int_0^{a_3} \Gamma_3 \cdot d \log a_3,$$

* Butler and Ockrent, J. Physical Chem., 34, 2841, 1930.

and if the solution is dilute we may substitute for Γ_3 the value of ν_3 given by (246). We thus obtain

$$\begin{split} \rho &= \rho' - \frac{RT}{A_3} \int_0^{a_3} \frac{k_3 \cdot d\alpha_3}{1 + k_2 a_2 + k_3 a_3} \\ &= \rho' - \frac{RT}{A_3} \log \Big(\frac{1 + k_2 a_2 + k_3 a_3}{1 + k_2 a_2} \Big). \end{split}$$

The surface tension of the binary solution of S_2 alone, by (245), is

$$\rho'=\rho_0-\frac{RT}{A_2}\log{(1+k_2a_2)},$$

so that when $A_2 = A_3$, we have

$$\rho = \rho_0 - \frac{RT}{A_2} \log (1 + k_2 a_2 + k_3 a_3). \dots (247)$$

Butler and Ockrent found that the surface tension of solutions of ethyl and propyl alcohols, and of propyl alcohol and phenol, were in agreement with these equations.

Standard Free Energies in the Surface Layer. Traube's Rule. We shall now see if it is possible to proceed further on thermodynamical lines by expressing the partial free energy of an adsorbed substance as a function of the amount adsorbed. If the distribution of the adsorbed substance near the interface is unknown it is probable that no useful result could be obtained by this procedure, but if the adsorbed molecules are all related in the same way to the underlying phase, e.g. if they are all in the surface layer, a comparatively simple formulation can be made. The partial free energies of the components, as determined by Gibbs's method, are the same throughout the surface region as in the homogeneous phases with

which they are in contact. Expressing the partial free energy of the adsorbed substance S_2 as a function of Γ_2 by

$$\bar{F}_{2(\text{surface})} = \bar{F}^{\circ}_{2(s)} + RT \log f(\Gamma_2),$$

where the form of $f(\Gamma_2)$ is to be determined, and expressing the partial free energy in the underlying solution by

$$\bar{F}_{2 \text{ (solution)}} = \bar{F}^{\circ}_{2} + RT \log \alpha_{2},$$

we have, since the partial free energies in the surface layer and in the solution must be the same,

$$\bar{F}^{\circ}_{2(8)} + RT \log f(\Gamma_{2}) = \bar{F}^{\circ}_{2} + RT \log \alpha_{2},$$

$$RT \log \frac{f(\Gamma_{2})}{\alpha_{2}} = \bar{F}^{\circ}_{2} - \bar{F}^{\circ}_{2(8)}. \quad \dots (248)$$

or

Now we have seen that when the adsorbed molecules are all located in the surface layer, Langmuir's equation,

$$\frac{A_2 \nu_2}{1 - A_2 \nu_2} = k \alpha_2,$$

not only gives approximately correct values of the adsorption, but also, when used in conjunction with Gibbs's equation, gives rise to Szyszkowski's equation, which represents fairly closely the variation of the surface tension with the concentration. Since (248) requires that $f(\Gamma_2)/a_2 = \text{constant}$, if Langmuir's equation is to be satisfied $f(\Gamma_2)$ must be identified with $A_2\nu_2/1 - A_2\nu_2$. We may therefore write

$$\bar{F}_{2 \text{ (surface)}} = \bar{F}^{\circ}_{2 \text{ (s)}} + RT \log \frac{A_2 \nu_2}{1 - A_2 \nu_2}, \dots (249)$$

substituting this value of $f(\Gamma_2)$ in (248), it is evident that

$$RT \log k = \bar{F}^{\circ}_{2} - \bar{F}^{\circ}_{2(s)}, \dots (250)$$

where k is the constant of Langmuir's and Szyszkowski's equations.

We have seen that, in accordance with Traube's rule, k increases in an approximately constant ratio as we pass up as homologous series of aliphatic compounds, *i.e.* $RT \log k$ increases by approximately constant increments. The average value of k_{n+1}/k_n derived from the normal aliphatic acids is 3·5 and the corresponding increment of $RT \log k$ is 750 calories. We can therefore express the values of $\bar{F}^{\circ}_{2} - \bar{F}^{\circ}_{2(s)}$ for the members of a homologous series approximately by

$$\bar{F}^{\circ}_{2} - \bar{F}^{\circ}_{2(s)} = K + 750C,$$

where K is a constant and C the number of carbon atoms in the molecule. Now \overline{F}°_{2} is the standard free energy of the solute in dilute aqueous solution. If $F^{\circ}_{2(l)}$ is the free energy of the pure solute as a liquid, it has been shown (p. 90), that $\overline{F}^{\circ}_{2} - F^{\circ}_{2(l)}$ also increases by approximately constant increments as we pass up as homologous series and the average increment for the aliphatic alcohols is 800 calories, *i.e.*

$$\bar{F}^{\,\circ}_{2} - F^{\,\circ}_{2\,(l)} = K' + 800\,C.$$

It follows that $\bar{F}^{\circ}_{2(8)}$ and $\bar{F}^{\circ}_{2(l)}$ differ by an amount which is approximately constant or changes to a much smaller extent than either

$$\overline{F}^{\circ}_{2} - F^{\circ}_{2(l)}$$
 or $\overline{F}^{\circ}_{2} - F^{\circ}_{2(s)}$.

A qualitative idea of the meaning of this can be obtained as follows. $\bar{F}^{\circ}_{2(s)} - F^{\circ}_{2(l)}$ is a measure of the work required to transfer the solute from its pure liquid to the surface layer of an aqueous solution. If the adsorbed molecules are arranged with their "polar" or "watersoluble" groups (-OH, -COOH, etc.) in the surface layer of the solution and their hydrocarbon chains pointing outwards, this quantity will be mainly the free

energy of interaction of water with the active group and will be constant for each homologous series of compounds. On the other hand, $\bar{F}^{\circ}_{2} - F^{\circ}_{2(l)}$, which is a measure of the work required to bring the whole molecule into the solution increases steadily with the length of the hydrocarbon chain. In other words, $\bar{F}^{\circ}_{2(s)} - \bar{F}^{\circ}_{2(l)}$ is the free energy of solution in the water of the "polar" groups of the molecules only, while $\bar{F}_{2}^{\circ} - F_{2(l)}^{\circ}$ is the free energy of solution of the whole molecule. Traube's rule arises because the former is constant for a given group, while the latter increases by a constant amount for each additional - CH2 group.

Writing as an approximation $\overline{F}_{2(8)}^{\circ} - F_{2(l)}^{\circ} = \text{constant}$, (250) becomes

$$RT \log k = \overline{F}^{\circ}_{2} - F^{\circ}_{2(l)} - \text{const.},$$

or, by (134),

$$RT \log k = RT \log f_2^{\circ} - \text{const.},$$

where f_2° is the activity coefficient of the solute in very dilute aqueous solution. We thus see that there is a very close parallelism between the surface activity of a solute as measured by k and its activity coefficient in dilute aqueous solution. Since in the case of slightly soluble substances the solubility N_2 is the reciprocal of f_2 , the same parallelism is found between k and $1/N_2$.

Equations of State for the Surface Layer. A number of semi-empirical equations have been suggested for the relation between the surface tension produced by a solute and the amount adsorbed. Traube * found that for very dilute solutions the lowering of the surface tension was proportional to the concentration of the solute in the solution, i.e. $\rho_0 - \rho = km$. Writing $\rho_0 - \rho = \phi$, and taking

^{*} Lieb. Annalen, 255, 27, 1891.

the activity coefficient of the solute as unity, we have by Gibbs's equation

$$\Gamma = \frac{-d\rho}{RT \cdot d \log m} = -\frac{d\rho}{dm} \cdot \frac{m}{RT} = \frac{\phi}{RT},$$
or $\frac{\phi}{RT \cdot \Gamma} = 1$. (251)

Traube suggested that the surface tension of the solution might be looked upon as the unaltered surface tension of the solvent (ρ_0) less the two dimensional "pressure" exerted by the adsorbed molecules in the surface layer owing to their thermal agitation. He therefore regarded (251) as analogous to the perfect gas equation

$$\frac{p}{RT \cdot c} = 1$$
,

where p is the pressure of c mols of a gas in unit volume. Schofield and Rideal * made a further examination of solutions from this point of view. $\phi/RT \times \Gamma$ was evaluated as $d \log a/d \log \phi$ (since $RT\Gamma = d\phi/d \log a$). Fig. 34 shows some curves of $\phi/RT\Gamma$ as obtained in this way, plotted against ϕ . Except in dilute solutions these quantities show a linear relation, which may be written

$$\frac{\phi}{RT \cdot \Gamma} = i + b\phi,$$

or $\phi\left(\frac{1}{\Gamma}-b\cdot RT\right)=iRT.$

By analogy with Amagat's equation, $p(v-v_0)=iRT$, $b \cdot RT$ can be regarded as the limiting area occupied by one mol of solute or $1/\Gamma_{\infty}$ where Γ_{∞} is the number of mols of solute in unit area of a completely covered surface.

^{*} Proc. Roy. Soc., A, 109, 57, 1925; 110, 167, 1926.

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We thus have

$$\phi\left(\frac{1}{\Gamma} - \frac{1}{\Gamma_{\infty}}\right) = iRT, \dots (252)$$

1/i increases in aliphatic compounds with the length of the hydrocarbon chain and is taken as a measure of the

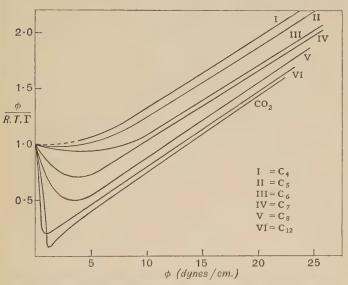


FIG. 34.— ϕ/RT . Γ for aqueous solutions of normal fatty acids. The curve for ${\rm CO_2}$ is that of pv/RT at 0° C. (After Schofield and Rideal).

lateral cohesion between adjacent molecules. This equation also applies to insoluble surface films of the gaseous type, ϕ being the surface "pressure," and $1/\Gamma$ the area of the film per molecule.*

Finally comparing (243) and (244), the following re-

^{*} See N. K. Adam, Physics and Chemistry of Surfaces, Chapter II.

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lation between ϕ and Γ is obtained from Szyszkowski's and Langmuir's equations:

$$\phi = -\frac{RT}{A_2}\log(1ka_2) = -\frac{RT}{A_2}\log(1 - A_2\Gamma_2). \quad (253)$$

A more profound thermodynamical deduction of an equation similar to this is given in the next section.

*Thermodynamics of a Monomolecular Surface Layer.

The free energy of a region containing an interface has been represented by the equation

$$F = \overline{F}_1 n_1 + \overline{F}_2 n_2 \dots + \overline{F}_n n_n + \sigma s,$$

where \bar{F}_1 , \bar{F}_2 are the partial free energies in the adjacent homogeneous phases, σ the additional free energy associated with unit area of the interface and s the surface area. We shall now enquire if there is any way of distributing the additional free energy σs among the molecules which are in or near the interface. There is no simple way of doing this unless the distribution of matter in the surface region can be precisely defined, but it has been shown that in cases in which the interface consists of a single layer of molecules, which alone differ in properties or proportions from the adjacent homogeneous phases, a solution can be obtained.*

Suppose that the two surfaces (Fig. 30) are drawn so that they contain between them only this surface layer of molecules. If n_1^s , n_2^s , etc., are the numbers of molecules $S_1, S_2...$ in the area s, we have

$$A_1 n_1^s + A_2 n_2^s + \ldots + A_n n_n^s = s.$$

A variation of the composition of the surface layer, at constant area, must therefore satisfy

$$A_1 dn_1^s + A_2 dn_2^s \dots + A_n dn_n^s = 0. \dots (254)$$

^{*} Butler, Proc. Roy. Soc., A, 135, 348, 1932.

We will consider the equilibrium between this surface layer and the adjacent homogeneous phases. If F^s is the free energy of the surface layer as so defined, its variation with the surface composition, when the surface area remains constant, can be represented by

 $(dF^s)_{T,P} = \mu_1^s dn_1^s + \mu_2^s dn_2^s + \dots + \mu_n^s dn_n^s \dots (255)$ μ_1^s , μ_2^s , etc., are quantities somewhat similar to partial free energies, but differing in that dn_1^s , dn_2^s , etc., are not independent, for if the surface area is kept constant, we cannot introduce more molecules of one kind without displacing some of those already present. The possible values of dn_1^s , dn_2^s , etc., are therefore subject to (254).

Similarly if F', F'' are the free energies of the two adjacent phases, containing the quantities n_1' , n_2' ; $n_1^{\prime\prime}$, $n_2^{\prime\prime}$, etc., of the components, we have

$$\begin{array}{ll} (d\,F')_{T,\,P} \,=\, & \bar{F}_{\,1}{'}\,dn_{1}{'} \,+\, & \bar{F}_{\,2}{'}\,dn_{2}{'} \,+\, \ldots\, +\, & \bar{F}_{\,n}{'}\,dn_{n}{'}, \\ (d\,F'')_{T,\,P} \,=\, & \bar{F}_{\,1}{''}\,dn_{1}{''} \,+\, & \bar{F}_{\,2}{''}\,dn_{2}{''} \,+\, \ldots\, +\, & F_{\,n}{''}\,dn_{n}{''}. \end{array}$$

For equilibrium between the phases it is necessary that $\bar{F}_{1}' = \bar{\bar{F}}_{1}''(=\bar{F}_{1}), \ \bar{F}_{2}' = \bar{F}_{2}''(=\bar{F}_{2}), \ \text{etc.} \ \text{We shall use as}$ the criterion of equilibrium, $\Sigma(\delta F)_{T,P} \geq 0$; i.e.

$$(dF^{s} - dF' - d\bar{F}'')_{T,P} = \mu_{1}^{s} dn_{1}^{s} \mu_{2}^{s} dn_{2}^{s} + \dots + \mu_{n}^{s} dn_{n}^{s} + \bar{F}_{1}(dn_{1}' + dn_{1}'') + \bar{F}_{2}(dn_{2}' + dn_{2}'') - \dots + \bar{F}_{n}(dn_{n}' + dn_{n}'') 0 \dots (256)$$

If none of the components can be formed out of others,

$$dn_1^s = -(dn_1' + dn_1''),$$

 $dn_2^s = -(dn_2' + dn_2''),$ etc.,

and therefore (256) becomes

 $(\mu_1^s - \bar{F}_1) dn_1^s + (\mu_2^s - \bar{F}_2) dn_2^s + \dots + (\mu_n^s - \bar{F}_n) dn_n^s \ge 0,$ for all possible values of dn_1^s , dn_2^s , etc., which must be in accordance with

$$A_1 dn_1^s + A_2 dn_2^s + \dots + A_n dn_n^s = 0.$$

These two equations can only be generally true if

$$\frac{\mu_1^s - \bar{F}_1}{A_1} = \frac{\mu_2^s - \bar{F}_2}{A_2} \dots = \frac{\mu_n^s - \bar{F}_n}{A_n}, \dots (257)$$

which is the condition of surface equilibrium.

Consider now a variation in which the surface area is increased by ds, the surface equilibrium being maintained. Writing $\nu_1 = n_1{}^s/s$, $\nu_2 = n_2/s$, etc., the numbers of molecules which enter the surface layer when its area is increased by ds are $dn_1{}^s = \nu_1 ds$, $dn_2{}^s = \nu_2 ds$, etc. The increase in the free energy of the surface layer is therefore

$$dF^s = \mu_1{}^s \nu_1 \, ds + \mu_2{}^s \nu_2 \, ds + \dots + \mu_n{}^s \nu_n \, ds,$$

while the change of the free energy of the homogeneous phases is

$$dF = -\bar{F}_1 v_1 ds - \bar{F}_2 v_2 ds - \dots - \bar{F}_n v_n ds.$$

The increase of the free energy of the system in the formation of an area ds of new surface is therefore

$$\begin{split} \rho = & dF^s + dF = (\mu_1{}^s - \bar{F}_1)\nu_1 \, ds \\ & + (\mu_2{}^s - \bar{F}_2)\nu_2 \, ds + \ldots + (\mu_n{}^s - \bar{F}_n)\nu_n \, ds. \end{split}$$

The work required for the formation of unit area of new surface under equilibrium conditions, is therefore

$$\rho = \frac{dF^s + dF}{ds} = (\mu_1^s - \overline{F}_1)\nu_1 + (\mu_2^s - \overline{F}_2)\nu_2 \dots + (\mu_n^s - \overline{F}_n)\nu_n.$$

Substituting the values of $(\mu_2{}^s - \bar{F}_2)$, etc., given by (257), we find that

$$\rho = (\mu_1^s - \bar{F}_1) \left(\nu_1 + \frac{A_2 \nu_2}{A_1} + \dots + \frac{A_n \nu_n}{A_1} \right),$$

or since $A_1\nu_1 + A_2\nu_2 + ... + A_n\nu_n = 1$, we have

$$\rho = \frac{\mu_1^s - \overline{F}_1}{A_1} = \frac{\mu_2^s - \overline{F}_2}{A_2} \dots = \frac{\mu_n^s - \overline{F}_n}{A_n} \dots \dots (258)$$

In order to obtain a relation between ρ and the surface composition it is necessary to have μ_1^s , etc., as a function of the latter. Since \bar{F}_1 is related with the composition of one of the homogeneous phases by

$$\bar{F}_1 = F_1^{\circ} + kT \log N_1 f_1 = F_1^{\circ} + kT \log a_1^{*}, \dots (259)$$

the author assumed that the variation of μ_1^s with the surface composition might be expressed by the similar equation $\mu_1^s = (\mu_1^s)_0 + kT \log N_1^s f_1^s$,(260)

where $N_1^s = \nu_1/\nu_1 + \nu_2 + ... + \nu_n$ is the molar fraction of S_1 in the surface layer and f_1^s an appropriate activity coefficient.

 $(\mu_1{}^s)_0$, which is the partial free energy of S_1 in a completed surface layer of the latter, must be supposed to be a function of the composition of the underlying liquid. Similar equations can be used for the other components.† Then (258) becomes

$$\begin{split} \rho = & \frac{(\mu_1{}^s)^\circ - F^\circ_1}{A_1} + \frac{kT}{A_1} \log \frac{N_1{}^s f_1{}^s}{\alpha_1}, \\ & \frac{(\mu_2{}^s)^\circ - F^\circ_2}{A_2} + \frac{kT}{A_2} \log \frac{N_2{}^s f_2}{\alpha_2} = \dots \text{ etc. } \dots \text{(261)} \end{split}$$

* The unit of quantity here is the molecule, hence k is the gas constant per molecule.

† The quantity $F_{2(surface)}$ of equation (249) really refers to the displacement in the surface layer by one mol of a solute of a quantity of the solvent which occupies an equal area. If the molecular areas of solvent and solute molecules in the surface are the same, $\bar{F}_{2(surface)} = \mu_2{}^s - \mu_1{}^s$. Using the values of (260), disregarding $f_1{}^s$, we have

$$\begin{split} \frac{G_{2}(surface)}{F_{2}(surface)} &= (\mu_{2}s)^{\circ} - (\mu_{1}s)^{\circ} + RT\log\frac{\nu_{2}}{\nu_{1}} \\ &= (\mu_{2}s)^{\circ} - (\mu_{1}s)^{\circ} + RT\log\frac{A_{2}\nu_{2}}{1 - A_{2}\nu_{2}}. \end{split}$$

which provides a rational basis for the expression used in (249).

or

or

*Derivation of Szyszkowski's Equation. If the surface is that of a binary solution of a solute S_2 in a solvent S_1 , $(\mu_1{}^s)^\circ$, $(\mu_2{}^s)^\circ$ are the partial free energies in completed layers of S_1 and S_2 on the surface of the solution. In dilute solutions the variation of the composition of the liquid underlying the surface layer may be supposed to be small and $(\mu_1{}^s)^\circ$, $(\mu_2{}^s)^\circ$ can be considered constant. In any case any variation of these quantities may be conveniently included in $f_1{}^s$, $f_2{}^s$. $f_1{}^s$ and $f_2{}^s$ are both taken as unity when $N_1{}^s=1$.

Then $\frac{(\mu_1^s)^{\circ} - F^{\circ}_1}{A_1} = \rho_0$ is the surface tension of the pure solvent, for which $N_1^s = 1$, $\alpha_1 = 1$, and we have

$$\rho = \rho_0 + \frac{kT}{A_1} \log \frac{N_1^s f_1}{a_1}, \dots (262)$$

which is similar in form to the Szyszkowski equation (253) and is completely equivalent to it when $A_1 = A_2$ and f_1^s and a_1 are unity.

When $A_1 = A_2$, (261) becomes

$$\log \frac{N_2^s f_2^s}{\alpha_2} - \log \frac{N_1^s f_1^s}{\alpha_1} = \frac{(\mu_1^s)^\circ - F_1^\circ - (\mu_2^s)^\circ + F_2^\circ}{kT},$$

$$\frac{N_2^s}{N_1^s} = \frac{\beta f_1^s}{f_2^s} \cdot \frac{\alpha_2}{\alpha_1}, \dots (263)$$

where $\beta = \exp$. $((\mu_1^s)^\circ - F_1^\circ - (\mu_2^s)^\circ + F_2^\circ)/kT$. When f_1^s/f_2^s is constant this is equivalent to Langmuir's equation (243).

Since $N_2^s = 1 - N_1^s$, $1/N_1^s = 1 + \frac{\beta f_1^s}{f_2^s} \cdot \frac{\alpha_2}{\alpha_1}$, and introducing this into (262), we have

$$\rho = \rho_0 - \frac{kT}{A} \log \left(\alpha_1 + \frac{\beta f_1^s}{f_2^s} \cdot \alpha_2 \right) f_1^s,$$

$$\rho = \rho_0 - \frac{kT}{A} \log \left(\alpha_1 + \beta' \alpha_2 \right) f_1^s, \dots (264)$$

where $\beta' = \beta f_1^s/f_2^s$. This modified form of Szyszkowski's equation has been found to apply with considerable accuracy over a wide range of the more concentrated solutions when β' and f_1^s are taken as constant. In these solutions the molar fraction of the solute in the surface layer is large, and it appears that f_1^s and f_2^s are practically constant. Table XLI shows the observed and calculated surface tensions for two cases.

TABLE XL.

CALCULATION OF SURFACE TENSIONS BY MODIFIED SZYSZKOWSKI EQUATION.

$$\rho = \rho_0 - \frac{kT}{A}\log(\alpha_1 + \beta'\alpha_2)f_1^s.$$

n	-Butyl Alcoh	ol.		Phenol.	
$\begin{array}{c} 2.303kT/A = 34.8, \\ \beta = 34, \ f_1{}^s = 0.68. \end{array}$		$\begin{array}{c} 2 \cdot 303kT/A = 34 \cdot 8, \\ \beta = 19, \ f_1{}^s = 0.90. \end{array}$			
a_2 . 0.0989 0.1928 0.3796 0.7119	ρ (calc.). 56·4 48·1 38·85 29·85	ρ (obs.). 56·31 48·08 38·87 29·87	a_2 . 0.06 0.10 0.16 0.20 0.30 0.40	$\begin{array}{c} \rho \text{ (calc.).} \\ 65.3 \\ 60.7 \\ 55.6 \\ 53.0 \\ 48.0 \\ 44.3 \end{array}$	$\begin{array}{c c} \rho \text{ (obs.).} \\ 65 \cdot 2 \\ 60 \cdot 6 \\ 55 \cdot 8 \\ 53 \cdot 0 \\ 48 \cdot 0 \\ 44 \cdot 2 \end{array}$

In more dilute solutions (264) fails to agree with the observed values of ρ , when $f_1{}^s$ and β' are given constant values. Table XLH shows the variation of $f_1{}^s$ with the concentration of dilute butyl alcohol solutions as calculated by (262). At present, however, there is insufficient data to make any generalisations about the activity coefficients in the surface layer.

TABLE XLI. $f_1{}^s \mbox{ for Butyl Alcohol Solutions}.$

a ₂ .	f_1s_*	N_1s .	
$0.0130 \\ 0.0258 \\ 0.05184$	0·91 0·89 0·81	0·80 0·65 0·43	
0.0989	0.70	0.24	

CHAPTER XI

GENERAL CRITERIA OF EQUILIBRIUM AND STABILITY

The Phase Rule. Each distinct kind of body which is present in a heterogeneous system is called a *phase*, but bodies which differ only in amount or shape are regarded as examples of the same phase.

Consider a single phase containing the quantities n_1 , $n_2, \ldots n_n$ of the independent components $S_1, S_2, \ldots S_n$, and having the entropy S and volume v. The phase is characterised by the n+2 intensity factors $t, p, \bar{F}_1, \ldots \bar{F}_n$. But these quantities are not all independent, for their variations are related by the equation

$$+SdT - vdp + n_1d\bar{F}_1 + n_2d\bar{F}_2 \dots + n_nd\bar{F}_n = 0.*\dots(265)$$

That is, if n+1 of the quantities $T, p, \bar{F}_1, \dots \bar{F}_n$ are varied, the variation of the last is given by (265). A

* Combining (42), which gives the variation of F with T and p, with (116), which gives the variation of F with n_1 , n_2 , etc., at constant T and p, we obtain

$$dF = -SdT + vdp + \overline{F}_1 dn_1 + \overline{F}_2 dn_2 \ \dots + \overline{F}_n dn_n.$$

Integrating this at constant T and p, we obtain

whence, instead of (118), in which T and p are supposed constant, we obtain

$$+SdT - vdp + n_1 d\overline{F}_1 + n_2 d\overline{F}_2 \dots + n_n d\overline{F}_n = 0.$$

$$249$$

single phase is thus capable of only n+1 independent variations, or we may say that it has n+1 degrees of freedom.

Now suppose that we have two phases in equilibrium with each other, each containing the same n components $S_1, \ldots S_n$. It is necessary for equilibrium that T, p, $\overline{F}_1, \ldots \overline{F}_n$ shall be the same in the two phases. But there are now two equations like (265), one for each phase. It follows that only n of these quantities can be varied independently, the variations of the last two being given by the two equations. The two phases have thus

$$(n+2)-2=n$$

degrees of freedom.

In general, if there are r phases each containing the same n components, there will be r equations like (265) between the variations of the n+2 quantities T, p, \overline{F}_1 , \overline{F}_2 , ... \overline{F}_n , which are the same throughout the system. Therefore only n+2-r of the quantities can be varied independently, and the number of degrees of freedom of n components in r phases is thus

$$\mathcal{F} = n + 2 - r. \dots (266)$$

This is the Phase Rule of Gibbs.

It does not matter if some of the components are absent from certain phases. Taking the system as a whole, we shall still have the n+2 quantities T, p, \bar{F}_1 , ... \bar{F}_n characteristics of the system and r relations like (265), which limit their variations. It is sometimes convenient to choose components which are not all independent of each other. Let n be the number of independent components, i.e. the minimum number of components in terms of which every variation of the system can be expressed. Let there be additional h components. These

components can be formed out of the others by reactions similar to that represented in (123), and for each such relation between the components there is a corresponding relation between their partial free energies, similar to (124). There will thus be h relations between the partial free energies like (124). The total number of variable quantities is n + h + 2, and the total number of relations between them h + r, so that the number of degrees of freedom is still

 $\mathcal{F}=n+2-r.$

We will briefly survey the application of the phase rule to some typical systems. In the first place, a system of one component in one phase has, by (266), two degrees of freedom. That is, there is a single relation like (265), viz. $+S \, dT - v \, dp + v_1 \, d\bar{F}_1 = 0$

between the three quantities T, p and \bar{F}_1 . Thus T and p can be varied at will, but for every value of T and p there is a corresponding value of \bar{F}_1 . Again, a single component in two phases has one degree of freedom, since there are two equations like (265) between the three quantities T, p, \bar{F}_1 . By means of these two equations we can get a relation between T and p. This relation is Clausius's equation, which was obtained in this way in Chapter I (eqn. 56). Finally, when a single component is present in three phases, there are three equations like (265) between dT, dp, and $d\bar{F}_1$, and therefore no variation is possible.

Again, a system of two independent components in a single phase has three degrees of freedom, *i.e.* if we give T and p certain values we cannot vary both \overline{F}_1 and \overline{F}_2 independently, but for every value of \overline{F}_1 there will be a corresponding value of \overline{F}_2 . In two phases this system

has two degrees of freedom. Therefore if we fix T and p no variation of the system is possible, *i.e.* so long as there are two phases \bar{F}_1 and \bar{F}_2 have constant values. Thus at a given T and p the two layers formed by water and ether have a definite composition and therefore definite values of \bar{F}_1 and \bar{F}_2 .

If there are three phases the number of degrees of freedom is only one. We can no longer fix arbitrarily the temperature and the pressure, but for every temperature there will be a fixed pressure. Thus if our three phases are ice—aqueous solution—vapour, the vapour pressure is completely determined at each temperature, and the relation between dp and dT can be obtained by solving the three equations like (265) between the four quantities dp, dT, $d\bar{F}_1$, $d\bar{F}_2$.

Application of Phase Rule to Systems containing Electrolytes. In applying the phase rule to systems containing electrolytes it is necessary, so far as the electrolytes are concerned, to take the number of independent components as one less than the total number of ions present. Suppose that altogether there are p ions in a system. In order to define the composition of every phase it is only necessary to state the amounts of p-1 ions, for the amount of the last ion can be determined by the condition that every phase must be electrically neutral. For example, in a system containing water and sodium, potassium, sulphate and chloride ions, the number of independent components is four, for the composition of every possible phase can be specified if we take as the components water and three of the ions. The amount of the fourth ion can then be determined by the condition that each phase is electrically neutral. Thus, if a solution contains x equivalents of Na⁺, y equivalents of K⁺ and z equivalents of SO_4^- , the amount of Cl⁻ must be x + y - z.

Since it is not possible to determine the partial free energy of individual ions in any phase, it is usual to take as the components, not p-1 of the ions but p-1 of the neutral salts which may be formed from them. Thus, in the above example, we may choose as the components, water and any three of the four salts NaCl, KCl, Na₂SO₄, K_2 SO₄, which can be formed from the ions. Not only can every variation of the composition of phases be expressed in terms of these components, but the state of each phase is also completely defined in terms of the partial free energies of the chosen components, for when the partial free energies of three of these salts is known that of the fourth is determined by the relation

$$ar{F}_{
m NaCl} + rac{1}{2} ar{F}_{
m K_2SO_4} = ar{F}_{
m KCl} + rac{1}{2} ar{F}_{
m Na_2SO_4}.$$

Conditions of Equilibrium with respect to Formation of New Phases. So far we have only determined the conditions which are necessary for the equilibrium of the phases originally present in a system. In order to determine whether a system is in equilibrium, it is necessary to show not only that the phases originally present are in equilibrium but also that no entirely new phases may be formed out of the phases originally present. The condition which must be satisfied for equilibrium in this respect is most readily found by criterion that if a system is in equilibrium, there is no possible change, at constant temperature and pressure, which causes a decrease in its free energy.

Consider a system containing the components $S_1, \ldots S_n$, which have in all the phases originally present the partial free energies $\bar{F}_1, \ldots \bar{F}_n$. Let dF be the free energy

of a small quantity of some other phase of the same components, at the same temperature and pressure, containing $dn_1, dn_2 \dots dn_n$ mols of $S_1, \dots S_n$. Then the condition of equilibrium with respect to the formation of this new phase, is

$$dF - \bar{F}_1 dn_1 - \bar{F}_2 dn_2 \dots - \bar{F}_n dn_n \ge 0. \dots (267)$$

For, suppose that this small quantity of the new phase is formed within the system. The free energy of the new phase is dF, while the change of the free energy of the original phases is $-\bar{F}_1 dn_1 - \bar{F}_2 dn_2 \dots - \bar{F}_n dn_n$. The quantity on the left of (267) thus represents the free energy change of the system in the formation of the given quantity of the new phase. If it is negative the new phase might be spontaneously formed within the system, and the system is therefore not in equilibrium with respect to its formation. The condition of equilibrium is therefore that this quantity shall be either zero or positive.

When a new body is formed within a system its quantity must at first be infinitesimally small. Unless a new body can be formed in infinitesimal quantities it cannot be formed at all. Consequently (267) may be regarded as the appropriate condition of equilibrium with respect to the formation of new phases.

We may therefore state the conditions of equilibrium of a heterogeneous system in the following way:

- (1) The partial free energy of every component must be the same in each of the original phases in which it is actually present.
- (2) (267) must be satisfied for every other phase of the same components at the same temperature and pressure.

If F is the free energy of an appreciable mass of the

new phase, containing the quantities $n_1, n_2 \dots n_n$ of the components, we might expect F to bear the same proportion to $n_1, n_2 \dots n_n$ as dF to $dn_1, dn_2 \dots dn_n$. In that case we could write (267) as

$$F - \bar{F}_1 n_1 - \bar{F}_2 n_2 \dots - \bar{F}_n n_n \ge 0. \dots (268)$$

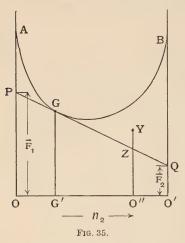
(The quantity on the left is the free energy change in the formation within the system of an amount of the new phase containing the quantities $n_1, n_2 \dots n_n$ of the components.)

This expectation however requires an important qualification. Usually, on account of the capillary forces, work has to be done to increase the degree of subdivision of a body. That is, the free energy of a small mass of a body is greater in proportion to its quantity than that of a large mass. That is, the proportion of dF to dn_1 , dn_2 , etc., is greater than that of F to n_1 , n_2 , etc. It follows that the quantity on the left of (267) will in general be greater than that in (268). Consequently when (268) is satisfied (267) will also be satisfied, and we may therefore use (268) as a practical test of equilibrium.

For the same reason it is possible for (267) to be satisfied when the expression of (268) is negative. That is, although the formation of an appreciable mass of the new phase would result in a decrease of free energy, the formation of a very small quantity may cause an increase of the free energy of the system, on account of the appreciable surface energy of very small bodies. The system will then be in equilibrium, but it will be an unstable equilibrium which can be destroyed by the addition of a comparatively small quantity of the new phase. This state of affairs appears to occur in cases of supersaturation.

Free Energy—Composition Diagrams. Gibbs described a valuable geometrical method of using the condition

(268), which we will illustrate by some simple examples. Consider a series of solutions of two components S_1 and S_2 .



Let n_1 be the quantity of the first, and n_2 that of the second component in a given solution. We will suppose that the quantity of the solution is such that $n_1 + n_2 = 1$; then n_1 and n_2 are equal to the molar fractions of S_1 and S_2 in the solution. Let F be the free energy of this quantity of the solution. Plotting F for a series of solutions at the same temperature and pressure against n_0 ,

we obtain the curve AGB (Fig. 35). Let PQ be the tangent to this curve drawn at the point G. Then by the method of intercepts (p. 66) it can be shown that the intercepts OP, O'Q made by this tangent on the axes are respectively equal to the partial free energies of S_1 and S_2 in the solution G, i.e. $OP = \bar{F}_1$, $O'Q = \bar{F}_2$. Therefore the points on the line PQ represent the values of $\bar{F}_1 n_1 + \bar{F}_2 n_2$ for any values of n_1 and n_2 for which $n_1 + n_2 = 1$.

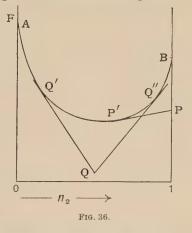
Now let there be another phase, for example a solid compound, of the same components in which their molar fractions are n'_1 , n'_2 . Let F' be the free energy, at the same temperature and pressure, of the quantity of this phase for which $n'_1 + n'_2 = 1$. This phase is represented by the point Y, where $OO'' = n'_2$, $O'O'' = n'_1$ and O''Y = F'.

Let Z be the point at which the vertical through O'' cuts the tangent PQ. Then $O''Z = n'_1\bar{F}_1 + n'_2\bar{F}_2$; and therefore $YZ = F' - n'_1\bar{F}_1 - n'_2\bar{F}_2$.

(In this equation F', n'_1 , n'_2 are determined by the phase Y; while \bar{F}_1 , \bar{F}_2 are determined by the phase G.)

The condition of equilibrium with respect to the formation of the given phase is $F' - n'_1 \bar{F}_1 - n'_2 \bar{F}_2 = 0$. This is satisfied if the point Y lies above or on the tangent line PQ. The condition of equilibrium of the phase G is thus that there shall be no other phase, at the same temperature and pressure, the free energy of which is represented by a point which lies below the tangent to the curve at the point G.

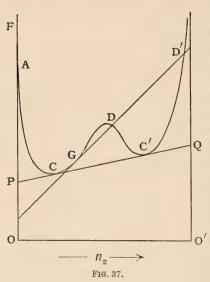
A phase which can co-exist with the given solution G must be represented by a point on the tangent PQ. In that case $\bar{F}' - n'_{1}\bar{F}_{1} - n'_{2}\bar{F}_{2}$ is zero, and the phase may be formed from the solution or may dissolve into the solution without any change of free energy. It is therefore in equilibrium with the In order to solution. find the composition of



the solution with which a given solid phase is in equilibrium we therefore draw a tangent from the point representing the solid to the free energy curve of the solution. Thus, if the point P (Fig. 36) represents the free energy of solid S_2 at the given temperature and pressure, the solution

with which it is in equilibrium is obtained by drawing the tangent PP' to the curve of the solution. The point of contact P' represents the solution which can co-exist with the solid phase. Again, let the free energy of a solid compound of the two components in equimolecular proportions be represented at the given temperature and pressure by the point Q. The points of contact of the two tangents QQ', QQ'' with the curve indicate the compositions of the two solutions with which the solid compound is in equilibrium.

Internal Stability of Binary Solutions. If the tangent drawn at a given point of the F-n curve of a series of



solutions cuts this curve, so that part of the curve lies below the tangent line, it follows from the reasoning of the previous section that the solution represented by the given point is unstable with respect to those solutions which are represented by points below the tangent line. For example, if the F-n curve of solutions of two components has the form ACGDC'D' (Fig. 37),

the tangent drawn at the point G cuts the curve at the points D and D'. The phase G is therefore un-

stable with respect to the solutions lying between D and D'.

It can easily be seen that the tangents at all the points between C and C', which are the points of contact of the common tangent PQ, will cut the curve, and therefore all the phases between C and C' are unstable. Moreover, since the points C and C' have a common tangent, the partial free energies of both components (represented by OP, O'Q) are the same in the two solutions represented by these points. These two solutions can therefore exist in equilibrium with each other, and are the limits of miscibility of the two components in each other. A system which contains the two components in proportions between the limits C and C', consists in its stable state of these two co-existent phases.

It can be seen from Fig. 37 that, although the solution G is unstable with respect to phases between D and D', it is stable with respect to the phases which lie between C and G and between G and D, since these phases lie above the tangent line at G. G is thus stable with respect to the phases which are adjacent to it. It is desirable to distinguish between phases which are unstable with respect to adjacent phases, and those which though stable with respect to adjacent phases are unstable with respect to some other phases of the same series of solutions. The latter though unstable might continue to exist unchanged for the formation of new phases might be prevented by effects similar to those which produce supersaturation; but the former cannot be expected to exist, for such effects cannot be expected to prevent the formation of a phase which differs only slightly from the original phase.

If a phase is stable with respect to adjacent phases it is evidently necessary that the points of the F-n curve

representing the adjacent phases shall lie above the tangent line at the point representing the given phase, as in

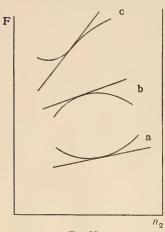


Fig. 38.

Fig. 38 (a). The F-ncurve must thus be convex from below at the given point. But if the phase is unstable with respect to adjacent phases the reverse holds as in Fig. 38 (b), i.e. the F-ncurve is concave from below at the given point. If the point representing the given phase is a point of inflexion of the F-ncurve, as in Fig. 38 (c), the curve will lie above the tangent line on one side

and below it on the other side. The given phase will then be stable with respect to the former phases and unstable with respect to the latter phases. The curve will be convex from below on one side of the given point, and concave from below on the other side, so that the given point will be the point which separates stable from unstable phases with respect to adjacent phases. The analytical statement of these conditions can easily be seen to be as follows:

Stability with respect to Adjacent Phases:

(1)
$$\frac{d^2F}{dn_2^2} > 0$$
; stable.
(2) $\frac{d^2F}{dn_2^2} < 0$; unstable.
(3) $\frac{d^2F}{dn_2^2} = 0$; limit of stability.

In Fig. 35 GG'=F, $O'Q=\bar{F}_2$ and the slope of the tangent PQ is $-dF/dn_1$. Therefore it can be seen that

$$\bar{F}_2 = F - n_1 \left(\frac{dF}{dn_1} \right)$$
.

(See p. 66 for a derivation of a similar equation.) Differentiating this with respect to n_2 we have

$$\frac{d\bar{F}_{2}}{dn_{2}} = \frac{dF}{dn_{2}} - n_{1} \left(\frac{d^{2}F}{dn_{1}dn_{2}} \right) - \frac{dF}{dn_{1}} \cdot \frac{dn_{1}}{dn_{2}},$$

or, since $dn_1 = -dn_2$,

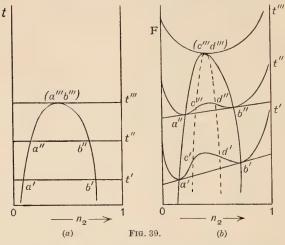
$$\frac{d\bar{F}_2}{dn_2} = n_1 \frac{d^2 F}{dn_2^2}.$$
 (270)

Since n_1 is necessarily positive the conditions of stability with respect to adjacent phases can thus be written in the form: if $d\bar{F}_2/dn_2 > 0$, the solution is stable; if $d\bar{F}_2/dn_2 < 0$, the solution is unstable; while if $d\bar{F}_2/dn_2 = 0$ the solution is at the limit of stability. Similar conditions can easily be obtained for $d\bar{F}_1/dn_1$. Therefore we can state that a solution is stable with respect to adjacent phases so long as the partial free energy of each component increases with its molar fraction, and is unstable when the partial free energy of each component decreases as its molar fraction is increased.

Critical Phases. Fig. 39 (a) shows the mutual solubilities of phenol and water as a function of the temperature. At the temperature t' the two phases of phenol and water which can exist in equilibrium with each other are represented by the points a' and b'. At a higher temperature t'' the corresponding points are a'' and b''. Ultimately, at t''', a critical temperature is reached at which the two phases which can co-exist become identical in composition. At higher temperatures phenol and

water are miscible in all proportions, i.e. the whole series of solutions from pure phenol to pure water can be obtained.

The F-n diagram for each of these temperatures is shown in Fig 39 (b). The two solutions which can coexist at a given temperature are those which have a common tangent on the F-n diagram for this tempera-



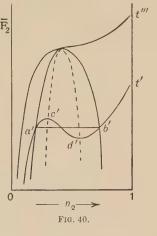
ture. Thus the compositions a', b' in Fig. 39 (a) are determined by the points at which the common tangent touches the corresponding curve in Fig. 39 (b). All the solutions represented by points on the curve between a' and b' are unstable, but if c' and d' are the points of inflexion of the curve, the solutions between a' and c' and between d' and b', which fall on parts of the curve which are convex from below, are not unstable with respect to adjacent phases and might possibly exist without change as supersaturated solutions. But the curve

between c' and d' is concave from below, and these solutions are unstable with respect to adjacent phases and cannot be expected to exist without change.

At the higher temperature t'' the F-n curve is similar, but points of contact of the common tangent a'' and b'' are closer together. As we approach the critical temperature it is evident that not only do the tangent points, but also the points of inflexion (c and d), approach each other and at the critical temperature they all become identical. The critical temperature is thus the temperature at which the undulation in the F-n curve just disappears.

The shapes of the curves of \bar{F}_2 , plotted against n_2 , are

thus as shown in Fig. 40, for temperatures corresponding to the F-n curves of Fig. 39. At t' the \bar{F}_2 curve has a maximum at c' and a minimum at d', and since between these points \bar{F}_2 decreases with increasing n_0 these solutions are unstable with respect to adjacent phases. As the critical temperature is approached the points c', d'approach each other and become identical at the critical temperature t'''. Thus, at the critical solution the \bar{F}_2 curve



is horizontal $(d\bar{F}_2/dn_2=0)$ and has a point of inflexion $(d^2\bar{F}_2/dn_2^2=0)$.

Above the critical temperature the F-n curve is everywhere convex from below, i.e. d^2F/dn_2^2 is everywhere

positive. Therefore by (270) $d\bar{F}_2/dn_2$ is also positive, so that \bar{F}_2 everywhere increases as n_2 is increased.

At the points of inflexion of the F-n curves it is evident that $d^2F/dn_2^2=0$. Now it can easily be seen that at the points of inflexion on the left (c',c''), dF/dn_2 has a maximum value, and, therefore, while d^2F/dn_2^2 is zero, d^3F/dn^3 is negative. Similarly, at the points of inflexion on the right dF/dn_2 has a minimum value, so that d^3F/dn_2^3 is positive. At the critical point, where the two points of inflexion become identical, d^3F/dn_2^3 cannot be other than zero, so that the critical point is characterised by the two equations:

$$\frac{d^2 F}{dn_2^2} = 0 \; ; \quad \frac{d^3 F}{dn_2^3} = 0 \; . \qquad (271)$$

Differentiating (270) with respect to n_2 , we have

$$\frac{d^2 \overline{F}_2}{d n_2}^2 = -\frac{d^2 F}{d n_2}^2 + n_1 \frac{d^3 F}{d n_2}^3.$$

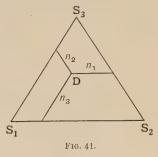
Therefore the equations (271) can be expressed as

and similar equations can of course be obtained for the other component.

Equilibrium and Stability of Ternary Solutions. The conditions of equilibrium in heterogeneous systems have been analysed in great detail by the use of these diagrams by Roozeboom in his great work, Die Heterogene Gleichgewichte vom Standpunkte der Phasenlehre, to which the student is referred for further information. It would take us too far afield to pursue this method in much greater detail, but it may be of interest to indicate very briefly its application to systems of three components.

Consider a solution which contains n_1 mols of S_1 , n_2 mols of S_2 and n_3 mols of S_3 , and suppose that the amount

is such that $n_1 + n_2 + n_3 = 1$. The composition of any such solution can be represented by a point in an equilateral triangle (Fig. 41), having sides of unit length, the apices of which represent the pure substances S_1 , S_2 , S_3 ; the sides the binary systems S_1S_2 , S_1S_3 and S_2S_3 , and the interior by the ternary solutions.

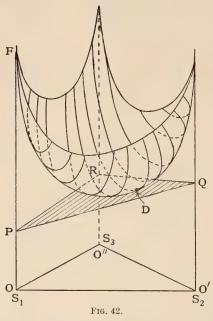


Thus, the values of n_1 , n_2 and n_3 for the point D are obtained by drawing lines parallel to the sides, n_1 being equal to the length of the line drawn from D to the side S_2S_3 , facing S_1 , etc.

The free energy F of any such solution can be represented by the vertical distance above the plane of the diagram at the point representing the composition of the given solution. We thus obtain for all the possible homogeneous solutions of the three components, at a given temperature and pressure, an F-n surface, such as is represented in Fig. 42.

In order to find the partial free energies of the components in any given solution we draw the plane which is the tangent to the F-n surface at the point representing the given solution. The intercepts made by this plane on the axes representing S_1 , S_2 and S_3 are equal to the partial free energies of these components. Thus in Fig. 42, if PQR is the tangent plane to the surface at the point D, OP, O'Q, O''R are equal to the values of \overline{F}_1 , \overline{F}_2 , \overline{F}_3 in the solution D.

The equilibrium of any solution is determined by the condition that there shall be no other phase of the same components at the same temperature and pressure, the free energy of which is represented by a point which lies



below the tangent plane drawn at the point representing the given solution. (This follows from (268). The proof, which is similar to that given for binary solutions, may be left to the reader.) As a consequence of this it is easy to see by the reasoning used in connection with binary solutions that:

(1) if the F-n surface is convex from below at a given point, *i.e.* if adjacent points of the surface lie above

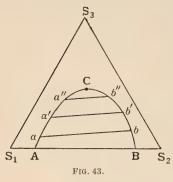
the tangent plane, the solution represented by that point is stable with respect to adjacent phases;

- (2) if the F-n surface is concave from below at a given point, i.e. if adjacent points of the surface lie below the tangent plane, the solution represented by that point is unstable with respect to adjacent phases;
- (3) if the F-n surface is convex from below at the given point, but the tangent plane drawn at this point cuts the F-n surface elsewhere, the solution is stable with respect to adjacent phases but unstable with respect to those solutions which lie below the tangent plane.

Thus, if the F-n surface is everywhere convex from below it lies above the tangent planes drawn at every point. Every solution represented on the surface is then stable with respect to all the other solutions. But if there is some other phase, such as a solid compound of the components, which is represented by a point which lies below the surface, some of the solutions will be unstable with respect to this phase, since the point will also lie below some of the tangent planes. The solutions with which the solid phase can co-exist can be determined by finding the points of contact with the surface of the tangent planes which also pass through the point representing the solid phase.

When the F-n surface is partly convex and partly concave from below it will not lie above every possible tangent plane. Some of the solutions will be unstable, and the stable state for these compositions will consist of two co-existent stable phases. The compositions of these two phases can be determined by rolling a tangent

plane over the surface so that it always has two points of contact; for when two points of the surface have



a common tangent plane the partial free energies of each of the components are the same in the two phases, which can therefore co-exist. Thus the curve ACB (Fig. 43) is the vertical projection on the triangular base of the points of contact of the common tangents to the F-n surface in such a case.

The connected points a and b, a' and b', etc., are the points of contact of common tangents and represent coexistent phases. These pairs of points approach each other, and ultimately become identical at the point C, which is the critical point for the mutual solubility of these substances. The solutions represented by points outside the curve ACB are all stable with respect to other solutions, but those inside are unstable with respect to adjacent or non-adjacent phases. The limit of stability with respect to adjacent phases is where the F-n surface ceases to be convex and becomes concave from below. The compositions at which this occurs would be represented by a curve inside ACB, the two branches of which also meet at the critical solution C. The critical solution is thus the point at which the concavity of the F-n surface just disappears. It is called the plait point, because a plait in the surface appears there and increases in extent (in the case illustrated) as we approach the S_1S_2 side of the triangle.

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